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Some comparisons of linear and branched-chain organopolysilanes

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SOME COMPARISONS OF LINEAR AND BRANCHED-CHAIN ORGANOPOLYSILANES

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INTRODUCTION

A vast amount of research has been conducted in the field of organopolysilanes since the initial studies by Kipping and co-workers. Until recently, almost all of the large number of polysilanes that had been characterized were linear or cyclic compounds. In sharp contrast to carbon chemistry, only two branched-chain polysilanes were reported in the literature prior to 1964.

The recent discovery of a convenient, direct procedure for the synthesis of some branched-chain organopolysilanes opened the door to a new and extremely promising area in organosilicon chemistry. It now appears that a large number of interesting, heretofore unavailable polysilanes can be synthesized by practical methods.

The objective of this work was to investigate preparative procedures for these novel branched compounds and to study their properties. Since comparative studies are always inherent in an investigation of this type, a number of linear organopolysilanes were synthesized. Also, some improved procedures were developed for the preparation of some previously described organopolysilanes.

It is hoped that the results of this work will help to stimulate further investigations in the area of branched-chain organopolysilanes.

HISTORICAL

Branched-chain Polysilanes

This review gives a detailed discussion of the chemistry of branched-chain polysilanes. Predominately all of the work in this area was conducted in these laboratories with in the past three years, and much of it has not appeared in the literature. The chemistry of non-branched polysilanes was the subject of several recent reviews (1-6). Thus this topic will be mentioned only briefly when it is necessary for a logical discussion of the branched compounds.

Non-organopolysilanes

The first branched-chain polysilanes were formed, along with a number of linear compounds, by the acid hydrolysis of magnesium silicide (7-11). This reaction was initially reported by Stock and co-workers (7,8); however, they were unable to isolate any of the branched isomers. Fehér, et al., (9) were the first to isolate the lowest branched homolog, tris(trisilyl)silane (I). Recent vapor phase chromatography studies (10, 11) indicated that an additional number of branched compounds were present in the mixture obtained from the hydrolysis of magnesium silicide.

$$Mg_2Si + H_3O^+ \longrightarrow \underset{\text{I}}{(H_3Si)_3SiH} + Si_nH_{2n+2}$$

Compound I was also prepared by Gokhale and Jolly (12) from silane by an ozonizer-type electric discharge method.

In 1964, Urry et al. (13-15) reported the synthesis of two interesting, highly-branched perchloropolysilanes, Tetrakis(trichlorosilyl)silane (II) and tetradecachloro-iso-hexasilane (III), were prepared by the amine catalyzed disproportionation of hexachlorodisilane or octachlorotrisilane.

$$4Si_2Cl_6 \longrightarrow \underline{neo}\text{-}Si_5Cl_{12} + 3SiCl_4 \quad (\underline{neo}\text{-}Si_5Cl_{12} = II)$$

$$3Si_3Cl_8 \longrightarrow II + 2Si_2Cl_6$$

$$5Si_2Cl_6 \longrightarrow \underline{iso}\text{-}Si_6Cl_{14}\cdot SiCl_4 + 3SiCl_4 \quad (\underline{iso}\text{-}Si_6Cl_{14}\cdot SiCl_4 = III)$$

$$Si_3Cl_8 \longrightarrow III + SiCl_4$$

Phenyl-substituted organopolysilanes

Tris(triphenylsilyl)silane (IV), the first branched organopolysilane, was reported (16) in 1959. Compound IV was synthesized (4%) *via* the reaction of triphenylsilyllithium with trichlorosilane. More recently, IV was prepared in somewhat higher yield (17%) by the treatment of trichlorosilane with triphenylsilylsodium.[1]

$$3PhSiM + Cl_3SiH \longrightarrow (Ph_3Si)_3SiH + Ph_6Si_2 \quad (M = Li, Na;\ (Ph_3Si)_3SiH = IV)$$

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[1] F. W. G. Fearon, Iowa State University of Science and Technology, Ames, Iowa. Information on the synthesis of some branched organopolysilanes. Private communication. 1966.

An attempt to prepare tetrakis(triphenylsilyl)silane by the treatment of tetrachlorosilane with four moles of triphenylsilyllithium gave hexaphenyldisilane as the only isolable product (16). A similar attempt to prepare this compound by the addition of triphenylsilylsodium to tetrachlorosilane was also unsuccessful.[1] However, in addition to hexaphenyldisilane, this latter reaction gave IV in ca. 4% yield. This unexpected product was probably formed by the hydrolysis of the corresponding silylsodium compound.

Another interesting branched compound containing the Si-H group, tris(dimethylphenylsilyl)silane (V), was synthesized (17) by the treatment of trichlorosilane with dimethylphenylsilyllithium (VI). Also, the reaction of VI with tetrachlorosilane and with methyltrichlorosilane gave tetrakis(dimethylphenylsilyl)silane and tris(dimethylphenylsilyl)-methylsilane (VIII), respectively (18).

$$Me_2PhSiLi + Cl_3SiH \longrightarrow (Me_2PhSi)_3SiH + (Me_2PhSi)_2$$
VI — V (10%) — IX

$$VI + SiCl_4 \longrightarrow (Me_2PhSi)_4Si + IX$$
VII (15%)

$$VI + Cl_3SiMe \longrightarrow (Me_2PhSi)_3SiMe + IX$$
VIII (32%)

Compound VII was prepared in lower yield (3.3%) via a one-step procedure involving the reaction of tetrachlorosilane with lithium and chlorodimethylphenylsilane (18). The treatment of tetrafluorosilane with

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[1] Ibid.

dimethylphenylsilyllithium also afforded a low yield (10%) of compound VII.[1] The major product from the reactions of VI with these polyhalosilanes was sym-diphenyltetramethyldisilane (IX).

$$4Me_2PhSiCl + SiCl_4 + 8Li \longrightarrow VII + IX$$

$$4Me_2PhSiLi + SiF_4 \longrightarrow VII + IX$$

Tris(trimethylsilyl)phenylsilane (X), another branched polysilane was isolated by Schwebke as one of the products from the reaction of decaphenylcyclopentasilane with lithium in the presence of chlorotrimethylsilane (19).

$$(Ph_2Si)_5 + Li \xrightarrow{Me_3SiCl} (Me_3Si)_3SiPh + Me_3Si(Ph_2Si)_nSiMe_3$$

By independent synthesis as shown in the sequence of equations below, Schwebke confirmed the idea that X was formed by the reaction of chlorotrimethylsilane with the silyllithium compound resulting from cleavage of a silicon-phenyl bond of bis(trimethylsilyl)diphenylsilane. The previously undescribed silyllithium compound, bis(trimethylsilyl)-phenylsilyllithium, was also characterized by hydrolysis to give bis-(trimethylsilyl)phenylsilane.

$$(Me_3Si)_2SiPh_2 + 2Li \longrightarrow (Me_3Si)_2SiPhLi \xrightarrow{H_3O^+} (Me_3Si)_2SiPhH$$

$$(Me_3Si)_2SiPhLi \xrightarrow{Me_3SiCl} X + Me_3SiPh$$

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[1] Ibid.

Permethylated organopolysilanes[1,2]

In 1964, Gilman and Smith reported (20) the first direct preparation of a branched-chain organopolysilane. Tetrakis(trimethylsilyl)silane (XI) was prepared in high yield by a one-step procedure involving the reaction of tetrachlorosilane with lithium and chlorotrimethylsilane. The discovery of this synthetic procedure initiated extensive and fruitful studies in this new area of organosilicon chemistry, and has led to the preparation of a large number of novel compounds that were heretofore unavailable.

$$4Me_3SiCl + SiCl_4 + 8Li \xrightarrow{THF} (Me_3Si)_4Si \quad (60\text{-}70\%)$$

A detailed study was undertaken to determine optimum conditions for the synthesis of this highly-branched compound. The best yields were obtained when a solution of tetrachlorosilane in THF was added to at least a 20% molar excess of the metal and chlorotrimethylsilane. The use of magnesium instead of lithium was found to be unsatisfactory for the synthesis of XI.

A mechanism was suggested which involves the formation of a series of silyllithium compounds, from the tetrachlorosilane moiety, which couple with chlorotrimethylsilane.

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[1] J. M. Holmes, Iowa State University of Science and Technology, Ames, Iowa. Information that is presented throughout this section on preparations and properties of branched polysilanes containing dimethylsilyl (HMe_2Si) groups. Private communication. 1965.

[2] C. L. Smith, Iowa State University of Science and Technology, Ames, Iowa. Information that is presented throughout this section on the synthesis and properties (18) of permethylated branched polysilanes. Private communication. 1966.

Subsequent to the preparation of tetrakis(trimethylsilyl)silane, this direct method was used for the synthesis of tris(trimethylsilyl)methylsilane (XII), tetrakis(dimethylsilyl)silane (XIII) and tris(dimethylsilyl)-methylsilane (XIV). Incidental to the preparation of XIII, a second highly-branched and symmetrical polysilane, hexakis(dimethylsilyl)disilane (XV), was isolated. Moreover, when a small amount of ethyl acetate was added to the reaction mixture, XV was the major product (ca. 30%). The exact role of the ethyl acetate was not known.

$$MeSiCl_3 + 4RMe_2SiCl + 6Li \longrightarrow (RMe_2Si)_3SiMe$$

XII, R = Me (40%)
XIV, R = H (46%)

$$SiCl_4 + 4HMe_2SiCl + 6Li \longrightarrow (HMe_2Si)_4Si + (HMe_2Si)_6Si_2$$

XIII, (55%) XV, (15%)

The reaction of trichlorosilane with lithium and chlorodimethylsilane gave a low yield (12%) of tris(dimethylsilyl)silane (XVI) and a larger quantity of XIII (31%). An attempt to prepare tris(trimethylsilyl)silane (XVII) by an analagous procedure afforded tetrakis(trimethylsilyl)silane (XI) as the only isolable product.

$$Cl_3SiH + 3HMe_2SiCl + 6Li \longrightarrow (HMe_2Si)_3SiH + XIII$$

XVI

$$Cl_3SiH + 3Me_3SiCl + 6Li \longrightarrow XI$$

$$\not\longrightarrow (Me_3Si)_3SiH$$

This one-step procedure proved to be unsatisfactory for the synthesis of phenyl-substituted polysilanes. For example, an

attempt to prepare tris(trimethylsilyl)phenylsilane (X) via the reaction of phenyltrichlorosilane with lithium and chlorotrimethylsilane gave a product resulting from reduction of the aromatic ring (18). The nature of this reaction is discussed in a following section.

Prior to the work by Smith and Holmes, those individual silylmetallic compounds which were readily available contained at least one phenyl group. Several unsuccessful attempts to prepare stable solutions of trialkylsilyl-alkali metal compounds have been reported and reviewed (2,3). Recently, a mixture of alkylsilyl and alkylsilanyl-alkali metal compounds were prepared by the treatment of decamethyltetrasilane with soduim-potassium alloy (21). Derivatization with chlorotrimethylsilane gave a mixture of linear methylated polysilanes.

$$Me_{10}Si_4 + Na\text{-}K \xrightarrow{Me_3SiCl} Me_3Si(Me_2Si)_nSiMe_3 \quad (n=0\text{-}3)$$

Dodamethylcyclohexasilane XVIII has also been a source of a mixture of alkylsilanyl metallic compounds. The treatment of XVIII with sodium-potassium alloy, followed by addition of chlorotrimethylsilane, gave a mixture of products (22) similar to that obtained from decamethyltetrasilane. West, et. al., found that XVIII is reduced by the same alloy with the subsequent formation of an anion radical (23).

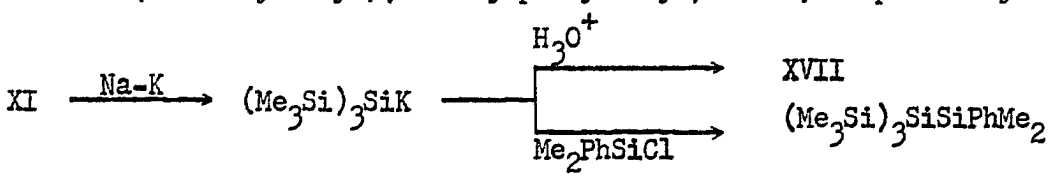
$$(Me_2Si)_6 + Na\text{-}K \longrightarrow (Me_2Si)_6^{-}M^{+}$$

Treatment of XVIII with methyllithium also afforded a mixture of silanyllithium compounds. Acid hydrolysis converted these to

the corresponding silicon hydrides which were detected by v.p.c. and infrared analyses.[1]

Although XVIII was unreactive towards lithium metal alone, extensive cleavage occurred when a catalytic amount of triphenylsilyllithium was added to the mixture of XVII and the metal (24). Under these conditions it appeared that the initial reaction was between the cyclosilanes (XVIII) and the silyllithium compound. The insoluble dimethylsilylene polymer, obtained incidental to the preparation of XVIII, however, did react with lithium metal alone to give a mixture containing silyllithium compounds (24).

As was the case with other permethylated polysilanes, an attempt to cleave tetrakis(trimethylsilyl)silane (XI) with lithium in THF was unsuccessful. However, when XI was treated with sodium-potassium alloy a slow reaction was observed. The resulting silylpotassium compound was characterized by derivatization with acid and with chlorodimethylphenylsilane to give tris(trimethylsilyl)silane (XVII) and tris(trimethylsilyl)(dimethylphenylsilyl)silane, respectively.



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[1] R. A. Tomasi, Iowa State University of Science and Technology, Ames, Iowa. Information on the treatment of XVIII with methyllithium. Private communication. 1962.

The reaction of XI with methyllithium in THF: ether (4:1) proved to be an excellent route (18,25) to tris(trimethylsilyl)-silyllithium (XIX). In a large number of runs, XIX was prepared in ca. 90% yield, essentially free of contamination. This method was subsequently used to prepare good yields of tris(dimethylsilyl)-silyllithium (XX) (25), bis(dimethylsilyl)methyllithium (XXI), bis(tri-methylsilyl)methylsilyllithium (XXII) and pentakis(dimethylsilyl)di-silanyllithium XXIII.

$(RMe_2Si)_4Si + CH_3Li \longrightarrow (RMe_2Si)_3SiLi + (CH_3)_3SiR$

XI, R = Me — XIX, R = Me

XIII, R = H — XX, R = H

$(RMe_2Si)_3SiMe + CH_3Li \longrightarrow (RMeSi)_2MeSiLi + Me_3SiR$

XIV, R = H — XXI, R = H

XII, R = Me — XXII, R = Me

$(HMe_2Si)_6Si_2 + CH_3Li \longrightarrow (HMeSi)_3SiSi(HMe_2Si)_2Li$

XV — XXIII

Compounds XIX and XX were also prepared by the reaction of phenyl-lithium and triphenylsilyllithium with XI and XIII, respectively. These reagents gave less satisfactory results than methyllithium. In the case of compounds XX, XXI and XXIII, the method of preparation is quite novel since organometallic reagents normally cause cleavage of Si-H bonds. In the preparation of XX, there was some indication that this reaction did occur to a small extent.

$$RM + R'_3SiH \longrightarrow R'_3SiR + MH$$

(M = Li or MgX)

The unusually high stability of the Si-H bonds of XIII toward organometallic reagents was further exibited by the observation that this compound did not react with phenylmagnesium bromide under conditions that this type reaction usually proceeds readily (26).

The stability of these silyllithium compounds in THF was studied by using the double titration (27) technique. Rate constants for the disappearance of some silyllithium compounds in THF are given below.

Table 1. Rate Constants for the Reaction of Some Silyllithium Compounds With THF at 25°

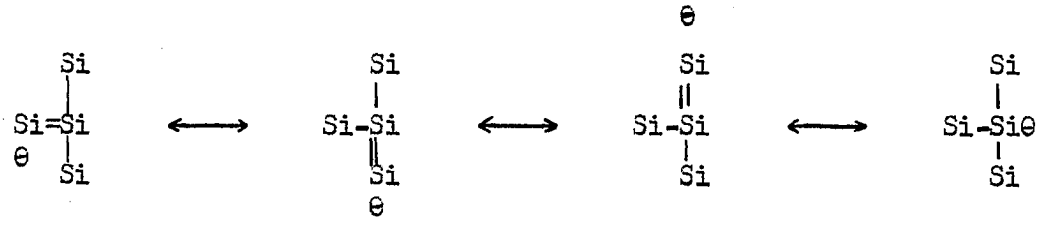
Compound	K x 10^3 $hours^{-1}$
$(HMe_2Si)_2MeSiLi$ (XXI)	27.01
$Ph_2MeSiLi$ (28)	2.1
$PhMe_2SiLi$ (28)	1.4
$(Me_3Si)_3SiLi$ (XIX)	1.3
Ph_3SiLi (28)	0.84
$(HMe_2Si)_3SiLi$ (XX)	0
$(Me_3Si)_2MeSiLi$ (XXII)[a,b]	——
$(HMe_2Si)_3SiSi(SiMe_2H)_2Li$[c]	——

[a] Rate constant was not calculated.

[b] Although no decomposition was observed during ca. 75 hrs., XXII was found to be less stable than XIX.

[c] No change in molarity during 190 hrs.

Table 1 shows that the branched silyllithium compounds, except XXI, are very stable in THF. It is also seen that XXI is the most unstable silyllithium species that has been studied. The relative stabilities of the branched compounds appear to be directly related to the degree of branching. This has been explained in terms of delocalization of the negative charge <u>via</u> $p_{\pi} - d_{\pi}$ bonding. This is clearly understandable if one considers the number of resonance structures available to the di- and trisilyl-substituted compounds.



<u>vs.</u>

The charge on the more highly branched compounds is more diffuse, thus resulting in a less reactive and more stable species.

Metalation of fluorene (29) was used to determine the relative reactivity of the branched silyllithium compounds. The trend in this property was the same as that of the stabilities.

These versatile branched silyllithium compounds were characterized by their conversion to a number of derivatives. Acid hydrolysis converted XIX, XX and XXII to the corresponding silicon

hydrides, XVII, XVI and the previously described (30) bis(trimethylsilyl)methylsilane, respectively.

$$\text{XIX} \xrightarrow{H_3O^+} \text{XVII}$$

$$\text{XX} \longrightarrow \text{XVI}$$

$$\text{XXII} \longrightarrow (Me_3Si)_2MeSiH$$

Derivatization of XIX and XX with trialkyl phosphates afforded good yields of the alkyl silanes.

$$\text{XIX} + (MeO)_3PO \longrightarrow (Me_3Si)_3SiMe \quad \text{XII}$$

$$\text{XX} + (RO)_3PO \longrightarrow (HMe_2Si)_3SiR$$

R = Me, XIV

R = iso-C_4H_9

Compounds XIX, XX and XXII were also reacted with a number of chlorosilanes. Very good yields (ca.65-70%) of the expected products were obtained. A tabulation of all branch-chain organopolysilanes is given in the following section.

Due to the instability and high reactivity of bis(dimethylsilyl-silyllithium (XXI), poor results were obtained when this compound was prepared or derivatized at room temperature. More satisfactory results were obtained when both the synthesis and subsequent reactions were carried out at temperatures between -50 and -20°

Evidence for the existence of pentakis(dimethylsilyl)disilanyllithium (XXIII) was afforded by its reaction with trimethyl phosphate to give pentakis(dimethylsilyl)methyldisilane in satisfactory yield.

$$\text{XXIII} + (MeO)_3PO \longrightarrow (HMe_2Si)_3SiSi(SiMe_2H)_2Me$$

Compounds XIX and XXII were reacted with carbon dioxide to obtain tris(trimethylsilyl)silanecarboxylic acid (XXIV) and bis(trimethylsilyl)methylsilanecarboxylic acid, respectively. These were then converted to the corresponding methyl esters by treatment with diazomethane.

$$\text{XIX} \xrightarrow[2)\ H_3O^+]{1)\ CO_2} (Me_3Si)_3SiCO_2H \xrightarrow{CH_2N_2} (Me_3Si)_3SiCO_2Me$$

$$\text{XXII} \longrightarrow (Me_3Si)_2MeSiCO_2H \longrightarrow (Me_3Si)_2MeSiCO_2Me$$

Like triphenylsilanecarboxylic acid (31), both XXIV and XXV undergo decarboxylation. Compound XXV decomposes at ca. 160° with the subsequent formation of sym-tetrakis(trimethylsilyl)dimethyldisiloxane. Decomposition of XXIV gave a mixture of products that were not characterized.

In addition to organolithium compounds, tetrakis(trimethylsilyl) silane (XI) was reacted with a number of other reagents. As expected, treatment with bromine, chlorine or phosphorus pentachloride caused cleavage of Si-Si bonds. However, the initially formed halogenated compounds reacted with these reagents at a rate comparable to that of XI. Thus, a complex mixture of halogenated compounds were always formed.

Compound XI reacted very slowly with lithium aluminum hydride (LAH), in refluxing THF, to form tris(trimethylsilyl)silane (XVII).

$$\underset{\text{XI}}{(Me_3Si)_4Si} + LAH \longrightarrow \underset{\text{XVII}}{(Me_3Si)_3SiH}$$

A mechanism was proposed which involves the formation of an intermediate containing a silicon-aluminum bond. A similar path was cited for the formation of triphenylsilane by the reaction of hexaphenyldisilane with lithium aluminum hydride (32).

An attempt was made to carry out a sulfuric acid demethylation of XI in a manner similar to that used with hexamethyldisilane (33). No reaction occurred until the mixture was heated to ca. 180°, at which time a violent fiery evolution of a gas was observed.

The branched organopolysilanes containing the tertiary Si-H group were found to posess some unusual chemical properties. During attempts to carry out spectral analyses on tris(dimethylphenylsilyl)-silane (V) in carbon tetrachloride, a complete reaction with the solvent was observed (17). The products were not isolated, but the disappearance of absorption due to the Si-H group and the detection of chloroform indicated that a chlorosilane was formed.

$$(PhMe_2Si)_3SiH + CCl_4 \longrightarrow (PhMe_2Si)_3SiCl + Cl_3CH$$

Although there had been several previous reports of the reaction of silicon hydrides with alkyl- and acylhalides, most of these required either long reflux periods or the use of aluminum chloride as catalyst. For a detailed review of this subject the reader is referred to several reviews (1,5,6). The only example of a facile reaction of this type is that involving the formation of halosilanes from silicon hydrides and triphenylmethylhalides (34,35). Corey and West (34) reported that some of these reactions were complete within a few minutes in solvents of high dielectric constant.

Smith (18) found that the silicon-hydrogen bond of XVII is unusually stable to cleavage by base. A high yield of unchanged XVII was recovered after treatment with aqueous base for ca. 12 hrs. Silicon-hydrogen bonds are generally very labile to cleavage by aqueous bases (1).

Chemical evidence indicated that the Si-H bond of XVII is more protonic than that of triphenylsilane. Since these bonds are polorized in the direction $Si^{+}H^{-}$ (1) the usual reaction of organolithium compounds with silicon hydrides is one of nucleophilic attack on silicon or electrophilic attack on hydrogen (1).

$$\text{n-BuLi} + Ph_3SiH \longrightarrow \text{n-BuSi}Ph_3 + LiH$$

This was taken as strong evidence for metalation of XVII via hydrogen-metal exchange.

Investigations are currently being conducted in these laboratories by Shiina[1] on improved procedures for the synthesis of certain branched-chain polysilanes. One of the principle reasons for the work is the discovery that during the direct synthesis of some branched compounds, using chlorotrimethylsilane, a significant quantity of the latter is converted to hexamethyldisilane. It is generally assumed that the reaction of chlorotrimethylsilane with lithium is

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[1] K. Shiina, Iowa State University of Science and Technology, Ames, Iowa. Information on improved procedures for the synthesis of some organopolysilanes. Private communication. 1966.

too slow to be useful for the preparation of hexamethyldisilane. However, Shiina has developed a convenient procedure for the synthesis of the disilane 60-70% yield from the chlorosilane and lithium in THF.

Physical properties

The completely symmetrical tetrakis(trimethylsilyl)silane XI is an unusually high melting (319-321°) waxy solid. In contrast, the normal isomer dodecamethylpentasilane, is a liquid at room temperature (36). Moreover, XI has a much higher melting point than hexacosamethyldodecasilane (m.p. 152°), the highest melting linear methylatedpolysilane (37). The unusual melting point of XI is undoubtedly associated with the high degree of symmetry in the molecule. This is evidenced by the fact that the unsymmetrical tetrasilylsilanes, $(Me_3Si)_3SiSiPh_nMe_{2-n}$ (n = 1,2), have melting points that are more than 100 degrees lower than that of XI.

Compound XI is also characterized by its high degree of volatility. Despite its high molecular weight, XI sublimes readily under reduced pressures. In fact, the sublimation technique is often used for the purification of XI. Although solids, the unsymmetrical tetrasilyl-substituted silanes $(Me_3Si)_3SiSiPh_nMe_{3-n}$ (n = 1-3), are also volatile (but not so volatile as XI) and can be conveniently analyzed by vapor phase chromatography. These phenyl-substituted tetrasilyl derivatives were found to possess unusual melting characteristics. The pure compounds appear to have melting point ranges. Smith (18) indicated that in this respect, this property resembles that of liquid crystals (38). For instance, these branch-

ed polysilanes form a turbid liquid which appears to be a mixture of liquid and solid. The appearance of the turbid liquid was recorded as the transition point, and the melting point that temperature at which a clear liquid developed (see Table 2 below).

Tris(trimethylsilyl)methylsilane (XII) is a low melting (57-59), sublimable solid that is best purified by distillation. The effect of symmetry on the melting point is again exhibited when it is noted that decamethyltetrasilane is a liquid (36). The unsymmetrical trisilyl derivatives of XII are liquids, except bis(trimethylsilyl)(triphenylsilyl)methylsilane, (m.p. 66-67°). A tabulation of the tri- and tetrasilyl-substituted organopolysilanes, except those containing the dimethylsilyl group, is given in Table 2.

Table 2. Branched-chain Organopolysilanes[a,b]

Formula	Name	M.p. (°C) (B.p./ mm.)
A. Trisilyl-substituted silanes		
$C_9H_{28}Si_4$	Tris(trimethylsilyl)silane	(80-83/ 8.0)
$C_{10}H_{28}O_2Si_4$	Tris(trimethylsilyl)silane-carboxylic acid	136[c]

[a] Compounds prepared in this work not included.

[b] Unless indicated otherwise, the compounds listed in this table were prepared by C. L. Smith (18).

[c] Was not obtained pure.

Table 2. (continued)

Formula	Name	M.p. (B.p./ mm.)
$C_{10}H_{30}Si_4$	Tris(trimethylsilyl)methylsilane	57-59
$C_{11}H_{30}O_2Si_4$	Methyl tris(trimethylsilyl)silanecarboxylate	96[c]
$C_{15}H_{27}Cl_5Si_4$	Tris(trimethylsilyl)pentachlorophenylsilane	126-127[d]
$C_{15}H_{32}Si_4$	Tris(trimethylsilyl)phenylsilane	(140/0.05)[e] sublimes
$C_{15}H_{32}Si_4$	Bis(trimethylsilyl)(dimethylphenylsilyl)methylsilane	(138-139/3.5)
$C_{20}H_{34}Si_4$	Bis(trimethylsilyl)(diphenylmethylsilyl)methylsilane	(148-151/0.8)
$C_{24}H_{34}Si_4$	Tris(dimethylphenylsilyl)silane	91-93

[d] K. Shiina, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the melting point of this compound. Private communication. 1966.

[e] Ref 19.

Table 2. (continued)

Formula	Name	M.p.(B.p./mm.) (°C)
$C_{24}H_{36}Si_4$	Tris(dimethylphenylsilyl)-methylsilane	53-54
$C_{24}H_{54}Cl_4Si_8$	1,4-Bis[tris(trimethylsilyl)]-tetrachlorobenzene[d]	242-261
$C_{25}H_{36}Si_4$	Bis(trimethylsilyl)(triphenyl-silyl)methylsilane	66-67
$C_{54}H_{46}Si_4$	Tris(triphenylsilyl)silane	206-207[f]
B. Tetrasilyl-substituted silanes		
$C_{11}H_{34}Si_5$	Tris(trimethylsilyl)(di methylsilyl)silane	Sublimes
$C_{12}H_{36}Si_5$	Tetrakis(trimethylsilyl)-silane	319-321[g]

[f] Ref. 16.

[g] In a sealed tube.

Table 2. (continued)

Formula	Name	M.p.(B.p./mm.)
$C_{17}H_{38}Si_5$	Tris(trimethylsilyl)(dimethylphenylsilyl)silane	190-190.5 185[h]
$C_{22}H_{40}Si_5$	Tris(trimethylsilyl)(dimethylphenylsilyl)silane	187-187.5 185[h]
$C_{27}H_{42}Si_5$	Tris(trimethylsilyl)(triphenylsilyl)silane	287-289 280[h]
$C_{32}H_{44}Si_5$	Tetrakis(dimethylphenylsilyl)silane	133-134

[h] Transition point.

Tetrakis(dimethylsilyl)silane (XIII), when freshly distilled, exists as a crystalline mass (m.p. 40-42°) which on agitation forms a thick slurry. Here again the high degree of symmetry seems to be responsible for the solid form of XIII. All of the known compounds of the type $H(CH_3)_2Si_nH$(n = 2,3,4,6) are liquids (5). Most of the other branched polysilanes containing the dimethylsilyl group are liquids. Table 3 gives a listing of these compounds along with some physical properties.

Those compounds containing only the H-Si and CH_3-Si groups were quickly oxidized when exposed to the atmosphere. Thus it was necessary to handle these under strictly anhydrous and oxygen-free conditions. Also, some compounds containing only these two groups ignited spontaneously when exposed to the atmosphere or spread out

on cloth or parer. A number of similar compounds $R_3Si(CH_3)HSi_nSiR_3$ (where R = H or Me and $n \geqslant 1$) and $(CH_3)HSi_n$ ($n \geqslant 5$) have been shown to ignite when spread in a thin layer and exposed to the air (39).

Table 3. Branched-chain Organopolysilanes Containing Dimethylsilyl-(HMe_2Si) Groups.[a]

Formula	Name	b.p. °C/mm. (m.p. °C)	$n_D^{20.3}$
A. Trisilyl-Substituted Silanes			
$C_6H_{22}Si_4$	Tris(dimethylsilyl) silane	60/5.0	1.4955
$C_7H_{24}Si_4$	Tris(dimethylsilyl) methylsilane	68/5.2	1.4950
$C_8H_{22}Si_4$	Bis(dimethylsilyl) (trimethylsilyl)methyl-silane	60/2.5	1.4895
$C_{10}H_{30}Si_4$	Tris(dimethylsilyl)-iso-butylsilane	80/2.0	1.5025
$C_{11}H_{32}Si_4$	Bis(dimethylsilyl) (triethylsilyl)methyl-silane	85/0.6	1.5106

[a] All compounds given in this table were characterized by J. M. Holmes, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. 1965.

Table 3. (continued)

Formula	Name	b.p.°C/mm. (m.p.°C)	$n_D^{20.3}$
$C_{13}H_{28}Si_4$	Bis(dimethylsilyl)-(methylphenylsilyl)-methylsilane	92/0.32	
B. Tetrasilyl-Substituted Silanes			
$C_9H_{25}Si_5$	Tetrakis(dimethylsilyl)silane	77/1.4 (40-42)	
$C_{12}H_{36}Si_5$	Tris(dimethylsilyl)-(triethylsilyl)silane	Sublimes (125-128)	
$C_{13}H_{30}Si_5$	Tris(dimethylsilyl)-(methylphenylsilyl)-silane	115/0.3	1.5635
$C_{14}H_{38}Si_5$	Tris(dimethylsilyl)-(dimethylphenylsilyl)-silane	101/0.01	1.5585
$C_{19}H_{34}Si_5$	Tris(dimethylsilyl)-(diphenylmethylsilyl)-silane	173/0.5	1.5940
$C_{21}H_{39}Si_5$	Tris(dimethylsilyl)-(triphenylsilyl)-silane	Sublimes (135-137.5	
C. Tri- and Tetrasilyl-substituted Disilanes			
$C_{11}H_{38}Si_7$	Pentakis(dimethylsilyl) methylsilane	110-120/0.04 (75-80)	
$C_{12}H_{42}Si_8$	Hexakis(dimethylsilyl)-disilane	(224)	

Spectral properties

The infrared (i.r.) and nuclear magnetic resonance (n.m.r.) properties of branched-chain organopolysilanes are very much the same as those of the non-branched compounds (5,40). Thus a detailed discussion at this time is not warranted. Interestingly, however, recent spectral studies (5) indicated that the position of i.r. bands for S-Ph and Si-H groups (17) depends on the branching in the compound. It was reported (40) that the SiPh group shows absorption bands in the 8.95-9.10 μ region. Lately, a number of tetrasilane derivatives have been found to show significant shifts in the position of this band (5). The frequency of absorption appears to be a function of the number of silyl groups substituted on the silicon atom bearing the phenyl group. The data given below illustrate this dependence (5).

	Band position μ
$Me_3SiSiPh_3$	9.02
$(Me_3Si)_2SiPh_2$	9.16
$(Me_3Si)_3SiPh$	9.23

A similar trend was observed for compounds containing the silicon-hydrogen bond. Table 4 gives i.r. and n.m.r. data for some compounds of this type. The n.m.r. data also show a shift in frequency in going from a primary to a tertiary silicon hydride. To explain the inconsistency observed with compound IV, it was reasoned (17) that the shift was opposed by the paramagnetic properties of the phenyl groups. The trends exhibited in Table 4 were thought to be associated with the electronegativity of the peripheral silicon

groups.

Table 4. Spectral Data for Some Compounds Containing the Si-H Group[a]

Compound	Si-H μ (CCl_4)	Si-H τ (CCl_4)
$Me_3SiSiPh_2H$	4.77	5.20
$(Me_3Si)_2SiPhH$	4.83	6.40
$(Me_3Si)_3SiH$	4.87	7.73[b]
$(Me_2PhSi)_3SiH$	4.88	7.32[b]
$(Ph_3Si)_3SiH$	4.85	5.89[b]

[a] Data taken from ref. 17.

[b] The solvent was carbon disulfide.

Recently, a great deal of work has been devoted to the study of ultraviolet properties of organopolysilanes (5,17,18,41-46). Although this work is still in its early stages, the use of u.v. spectral data for structure determinations appears extremely promising. A number of generalizations have been reported (5) as a result of the studies conducted thus far.

a) Phenyl-containing monosilanes exhibit only the benzenoid fine-structure of B-bands having low molar absorptivities.

b) With polysilanes, intense absorption maxima are observed and the λ_{max} increases with increasing chain length. The molar absorptivities also increase with increasing chain length.

c) Substituents such as Ph- and CH_2 = CH- cause an increase in the position of the $_{max}$, while Cl-, HO- and H- appear to have little effect on the band position. However, these latter groups do cause a change in the molar absorbtivity (43).

d) Cyclic and branched polysilanes absorb at lower wave lengths than their corresponding linear analogs.

Some typical examples illustrating the effect of branching are given in Table 5.

Table 5. Ultraviolet Spectral Data of Some Branched and Related Polysilanes.

Compound	λ_{max}, mμ (in cyclohexane)	Ref.
1. L $Me(Me_2Si)_3Me$	215	41,43
2. B $(Me_3Si)_3SiMe$ (XII)	207(shoulder)	18
3. B $(Me_3Si)_4Si$ (XI)[a]	—	18
4. L $Ph(Me_2Si)_3Ph$	236	41
5. B $(Me_3Si)_3SiSiMe_2Ph$	239	18
6. B $(Me_3Si)_3SiSiMePh_2$	238	18
7. L $H(Me_2Si)_3H$	218	43
8. B $(HMe_2Si)_3SiH$[a]	—	b

[a] No absorption above 210 mμ.

[b] J. M. Holmes, Iowa State University of Science and Technology, Ames, Iowa, Information on the spectral properties of some polysilanes. Private communication. 1965.

Table 5. (continued)

Compound			λmax, mμ (in cyclohexane)	Ref.
9.	B	$(HMe_2Si)_4Si$[a]	——	b
10.	B	$(HMe_2Si)_3SiSiMe_2Ph$	237	b
11.	L	$H(Me_2Si)_4H$	235.5	41
12.	B	$(HMe_2Si)_3SiSi(SiMe_2H)_3$[a]	——	b

Table 5 shows that the branched (B) compounds containing only the Si-Me and/or SiH groups absorb at much lower wave lenghts than the corresponding linear (L) compounds. However, substitution of phenyl for methyl or hydrogen (3 vs. 5 and 8 vs. 9) causes the position of the λ max for the branched compound to increase to a value which is about the same as that of the linear compound (4 vs. 5 and 4 vs. 9). Substition of additional phenyl groups on the same silicon atom (5 vs. 6) caused no additional shift in λmax.

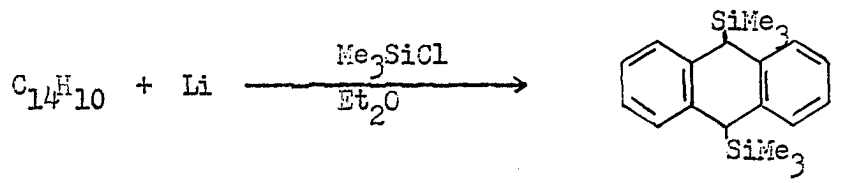
Anion Radicals in Organosilicon Chemistry

The synthesis of organoalkali metal compounds from olefins and alkali metals was initially reported by Schlenk and Bergmann (47). This early work involved the addition of metals to such compounds as anthracene, α ,ω-diphenylpolyenes and polyarylethylenes in diethyl ether.

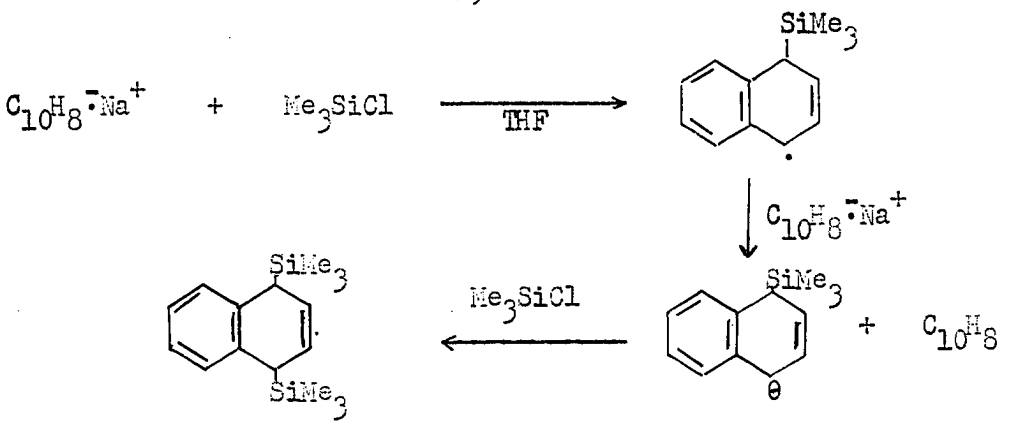
It was later found that these addition reactions take place much more readidly in THF and in ethers with a high oxygen to carbon

ratio such as 1,2-dimethoxyethane (48). This discovery greatly widened the scope of the application of anion radicals from olefins and aromatic hydrocarbons. Through the years, this general topic has been the subject of several excellent reviews (49-54).

Nearly all of the few reports on the reaction of hydrocarbon-alkali metal adducts with organosilicon compounds involve a chlorosilane trapping of an anion radical. A group of Russian workers (55,56) reacted the adducts of anthracene and naphthalene with a number of trialkylchlorosilanes to obtain disilylated derivatives. Although the product from the naphthalene reaction was indicated to be the 1,4-disilyl-1,4-dihydronaphthalene, no attempt was made to distinguish between 1,2- and 1,4-substitution in the structure.



Weyenberg and Toporcer later repeated this reaction using sodium or lithium in THF and isolated the 1,2- and 1,4-disilylnaphthalenes (57). These authors suggested a mechanism, shown below for the 1,4-isomer, involving an intermediate anion radical.



Similarily, a number of poly(disilyldihydronaphthalenes) were prepared by the reaction of alkali metal naphthalene adducts with chlorosilanes (58).

Although benzene gives no reaction under conditions that biphenyl and naphthalene form high concentrations of anion radicals (59,60), Weyenberg and Toporcer used chlorosilanes to trap short-lived species from benzene and substituted benzenes (61). Chlorotrimethylsilane, benzene and alkali metals gave 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene in 32 to 41% yields. A second product, 1,4-bis(trimethylsilyl) benzene was isolated in low yield from this same reaction. Benzene, lithium and chlorodimethylmethoxysilane, under the same conditions, gave 3,6-bis(dimethylmethoxysilyl)-1,4-hexadiene. Similarily, toluene and anisole afforded 30 and 50% yields of 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene and 1-methoxy-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene, respectively. The mechanism for these reactions were said to be similar to that given for naphthalene.

A group of Dow Corning chemists(62) reported the only examples in which more than two silyl groups were captured by anion radicals derived from a benzene nucleus. Chlorotrimethylsilane was added to a stirred

mixture of the sodium biphenyl adduct and excess sodium in 1,2-dimethoxyethane to give phenyltetra(trimethylsilyl)cyclohexene. A number of other chlorosilanes afforded the corresponding phenyltetrasilylcyclohexenes.

$R^1 = R^2 = Me$

$R^1 = Me,\ R^2 = C_2H_5$

$R^1 = Me,\ R^2 = C_6H_{13}$

$R^1 = Me,\ R^2 = C_5H_7$

$R^1 = C_2H_5,\ R^2 = \underline{n}\text{-}C_3H_7$

$R^1 = Me,\ R^2 = \underline{iso}\text{-}C_3H_7$

In a similar manner, the reaction of t-butylbenzene with lithium and chlorosilanes afforded t-butyltetrasilycyclohexenes (62). It was indicated[1] that one trimethylsilyl group was substituted on each of the four aliphatic ring carbons.

Two independent groups (63-65) established that phenyl-substituted silanes react with alkali metals to form anion radicals. Benkeser and co-workers (63), investigated the reaction of a number of phenylsilanes ($Me_{4-n}SiPh_n$, where n = 0-4 and others) with lithium in low molecular weight amines. It was reported that some of these com-

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[1] D. R. Weyenberg, Dow Corning Corp., Midlan, Michigan. Information on the synthesis and structure of some tetrasilylcyclohexenes. Private communication. 1966.

pounds consumed up to six equivalents of the metal per phenyl group. These reactions probably involved reduction of the aromatic ring in a manner similar to that determined for other substituted benzenes (64).

Solodovnikov and Chernyshev (65) found that several phenyl-substituted alkylsilanes and phenylsilanes react with potassium metal in 1,2-dimethoxyethoxyethane. Electron spin resonance studies showed that the following compounds formed anion-radicals.

$PhSiMe_3$	$PhSi(C_2H_5)_3$	$\underline{P}\text{-}Me_3SiC_6H_5SiMe_3$
A	B	C
$PhCH_2SiMe_3$	$Ph(CH_2)_2SiMe_3$	$Ph(CH_2)_3SiMe_3$
D	E	F

It was reported that A - C form very stable radicals and that those from D - F were less stable. Moreover, the stabilities decreased with an increase in the number of methylene groups. It was therefore deduced, (65) that the stability is caused by d_{π}-p_{π} interactions of the empty silicon orbitals and the electrons of the phenyl groups.

Despite the findings by these two groups, the only reported examples in which the trapping of anion-radicals from phenylsilanes was put to synthetic use are those afforded by the preparation of pentasilylcyclohexenes in these laboratories during the course of this study (see Discussion section).

Weyenberg, et al., synthesized a number of disilylalkanes, containing one or two reduced olefin units, by the reaction of alkali metal adducts of aryl olefins with chlorosilanes (66). Styrene and

chlorotrimethylsilane gave phenyl-1,2-bis(trimethylsilyl)ethane and 1,4-bis(trimethylsilyl)butane. Methylstyrene afforded the corresponding 2-phenyl-1,2-disilylpropane and 2,5-disilylhexane. These products were isolated in 65-90% yields.

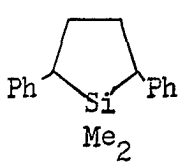
$$Me_3SiCl + PhRC{=}CH_2 + M \xrightarrow[THF]{} Me_3SiCPhRCH_2SiMe_3 + (Me_3SiCHPhRCH_2)_2$$

(M = Na, Li) (R = H, CH_3)

The ratio of monomolecular disilylation varied with the condition under which the syntheses were conducted. The change in ratio of silane to olefin in the reactions with lithium in THF was particularly noticeable. A 1:1 ratio of silane to olefin greatly favored bimolecular disilylation (ca. 81%), whereas a 2:1 or higher ratio of silane to olefin favored monomolecular disilylation (ca. 75%).

These disilylation reactions were also carried out with chlorodimethylsilane and chlorodimethylmethoxysilane (66). In addition to the expected products, the methoxysilane and styrene also gave 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane in 20% yield. This cyclic product was also prepared by the reaction of styrene with lithium and dichlorodimethylsilane (66).

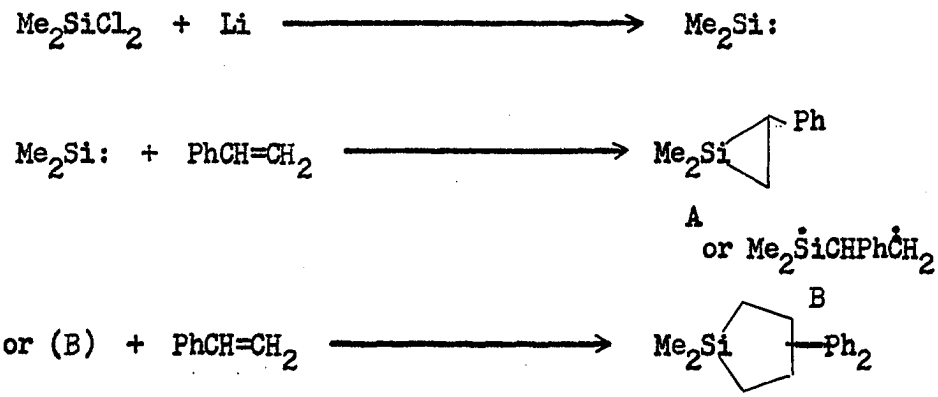
$$2PhCH{=}CH_2 + Me_2SiCl_2 + 2Li \longrightarrow$$



Weyenberg and co-workers indicated that the scheme which correlates all of the data on the disilylation reactions involve the trapping, via reaction with a chlorosilane, of an anionic species

formed from the unsaturated organic compound and alkali metal.

The reaction with lithium styrene and dichlorodimethylsilane had previously been run by a group of Russian chemists (67-69), who isolated a cyclic compound with the same properties as Weyenberg's product. Interestingly, however, the Russian authors suggested a mechanism which involves an initial reaction between the chlorosilane and alkali metal to form a divalent silicon intermediate.



The data reported (66) by Weyenberg indicated that the isolation of the silacyclopentane is of limited merit in establishing the intermediacy of divalent silicon species, as suggested by the Russian chemists.

Eisch has shown (70) that solutions of lithium-biphenyl complexes in tetrahydrofuran are very effective in promoting cleavage of carbon-heteroatom linkages under conditions that the reactions with the metal alone proceed very slowly or not at all. It was also found (70) that catalytic quantities of biphenyl in the presence of the metal were frequently effective. The use of these complexes as a

source of soluble lithium metal offers several advantages over the use of the metal alone.

Analagous results had been reported by Coates and co-workers (71) who prepared solutions of triphenylstannylsodium by the action of sodium naphthalenide on hexaphenyldistannane, tetraphenylstannane or bromotriphenylstannane.

Similarily, Fearon (72) has shown that triphenylsilylsodium can be prepared by the treatment of triphenylsilane, hexaphenyldisilane, or chlorotriphenylsilane with sodium naphthalenide.

$$Ph_3SiR + C_{10}H_8{:}Na^+ \longrightarrow Ph_3SiNa$$

(R = H, Cl, Ph_3Si)

Triphenylsilylsodium had previously been prepared by the cleavage of hexaphenyldisilane in 1,2-dimethoxyethane (73) and in liquid ammonia (74). However, in the ethereal solvent this compound is difficult to prepare and unstable, whereas in liquid ammonia the silylsodium compound is rapidly protonated by the solvent. Thus, the reactions with sodium naphthalenide (72) represent an excellent route to triphenylsilylsodium.

It was also indicated that Trainor obtained evidence for metalation of triphenylsilane by the lithium-biphenyl complex.[1]

In an interesting study, Fearon (72) investigated the reaction of some triphenylsilyl halides with the sodium naphthalenide adduct to

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[1] J. J. Eisch, The Catholic University of America, Washington, D. C. Information on the unpublished thesis work of J. T. Trainor at the University of Michigan. Private communication. 1966.

determine whether such a system could provide a useful source of the triphenylsilyl radical. The expected reaction was electron transfer between the hydrocarbon anion radical and the silyl halide. Reactions with the chloro- or fluorosilane gave hexaphenyldisilane (70-80%) as the major product. There was also isolated small amounts of 1,4-bis-(triphenylsilyl)-1,4-dihydronaphthalene and 1-naphthyltriphenylsilane. Lithium naphthalenide gave similar results. The data from this study

$$C_{10}H_8\cdot M^+ + Ph_3SiX \longrightarrow Ph_6Si_2 + \text{others}$$

indicated that the formation of most products could be explained by mechanisms involving an intermediate triphenylsilyl radical.

Investigations are currently being conducted in these laboratories to determine the usefulness of aromatic hydrocarbon alkali-metal adducts in the area of silicon chemistry. Fearon has found that catalytic quantities of naphthalene or biphenyl in the presence of excess metal, are very effective in causing cleavage of the Si-Si bond of hexaphenyldisilane and 1,2-dimethyltetraphenyldisilane.[1] The resulting silylmetallic compounds were formed in very high yields. In contrast, under the same conditions, 1,2-diphenyltetramethyl disilane gave compounds resulting from addition of phenyldimethylsilyl groups to the aromatic ring. The silylsodium compound could not be detected. Preliminary results indicated[1] that the chemical properties of these

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[1] F. W. G. Fearon, Iowa State University of Science and Technology, Ames, Iowa. Information on the use of aromatic hydrocarbons in the formation of silylmetallic compounds. Private communication. 1966.

$$(RPh_2Si)_2 + 2M \xrightarrow[THF]{C_{10}H_8} 2RPh_2SiM$$

R = Ph, Me
M = Na, Li

heretofore unavailable silylsodium compounds are not completely analagous to those of the corresponding silyllithium species. It was particularily noticeable that less halogen-metal exchange (3) occurred with the sodium compounds.

The role of the hydrocarbon in the formation of silylmetallic compounds will be discussed along with the presentation of the author's work in this area.

EXPERIMENTAL

The solvents and reagents used in the following experiments were commercially available materials. Tetrahydrofuran (THF) was dried either by refluxing over sodium metal followed by distillation from lithium aluminum hydride immediately before use, or by storage over sodium wire. Anhydrous grade diethyl ether was stored over sodium prior to use. Petroleum ether refers to that fraction boiling over the 60-70° range.

Lithium was obtained from the Lithium Corporation of America or the Foote Mineral Company. The organosilicon halides were supplied by the Union Carbide Corporation or purchased from the Dow Corning Corporation. Organometallic species were quantitatively titrated according to a published (27,75) double titration technique, using allyl bromide or 1,2-dibromoethane.

In general, the experimental apparatus consisted of a three-necked standard tapered flask equipped with a Trubore stirrer, a Friedrichs condensor and an addition funnel. In the case of heterogenous reactions, a high speed air-driven motor and a Hershberg stirrer were used to effect more efficient agitation. The terms "rapidly stirred" or "rapid stirring" will be used to indicate that the Hershberg stirrer and air-driven motor were employed. All glassware was oven-dried and purged while hot with dry, oxygen-free nitrogen before used. Color Test I (18,76,77) was used as a qualitative test for organometallic reagents.

Molar refractions were determined using recently published data (1). All boiling and melting points are uncorrected. The latter values were determined using a Mel-Temp apparatus. Molecular weight determinations were obtained with a vapor pressure osmometer, Model 301A, manufactured by Mechrolab. Inc., Mountain View, California. Benzil was used as standard with benzene as solvent.

Infrared (i.r.) spectra were routinely determined using a Perkin-Elmer, Model 21, spectrophotometer. For the identification of organosilicon compounds, the infrared correlations of Smith (40) were used. The intensity of infrared bands are reported as: s(strong) m(medium), and w(weak). The ultraviolet (u.v.) spectra were determined in cyclohexane with a Beckman DK-2A spectrophotometer. Proton magnetic resonance (n.m.r.) spectra were obtained with a Varian Associates Spectrometer, Model A-60. Vapor phase chromatographic (v.p.c.) analyses were carried out using a F & M Model 500 Gas Chromatograph with 18-24 in. columns packed with Silicone gum rubber on Chromosorb W (1:20).

Direct Synthesis of Some Linear and Branched Polysilanes

Tetrakis(trimethylsilyl)silane

Tetrakis(trimethylsilyl)silane was the starting material in many of the reactions carried out during the course of this study. This compound was prepared in good yield (50-65%) by essentially the same procedure reported by Gilman and Smith (20,78). A typical run is described at this time.

Twenty milliliters of a solution of 74 g. (0.44 mole) of tetrachlorosilane in 150 ml. of THF was added at once to a mixture of 284 g. (0.264 mole) of chlorotrimethylsilane, 32 g. (4.5 g.-atoms) of lithium and 350 ml. of THF. This mixture was stirred for ca. 5 min. to initiate an exothermic reaction. The remainder of the solution was then added during 8 hours. Subsequent to 30 hours of stirring, the reaction mixture was filtered from the excess lithium, hydrolyzed and worked up as usual. Removal of the organic solvents gave a semi-solid residue which was taken up in 95% ethanol, cooled at 0° for 1 hr. and filtered to give 92 g. of the crude product. Sublimation (ca. 75°/0.01mm.) afforded 86.5 g. of tetrakis(trimethylsilyl) silane, m.p. 310-316° (in a sealed tube, and the apparatus was preheated to 300°). Recrystallization from ethyl acetatemethanol gave a total of 84 g. (60.1%) of the pure product, m.p. 318-321°, (lit. value (18,78) 319-321°).

Tris(trimethylsilyl)methylsilane and
sym-Tetrakis(trimethylsilyl)dimethyldisilane

Run 1. To a rapidly stirred mixture of 75 g. (1.07 g.-atoms) of lithium, 490 g. (4.5 mole) of chlorotrimethylsilane and 600 ml. of THF was added 25 ml. of a solution of 210 g. (1.41 mole) of methyltrichlorosilane in 250 ml. of THF. After 5 min. the remainder of the solution was added during 9 hours. The reaction was continued for a total of 24 hours and the mixture was filtered from the excess lithium. After hydrolysis the organic layers were separated and dried over anhydrous sodium sulfate. Subsequent to the removal of the volatiles, the residue was fractionated to give 47.5 g. of impure

material and 131.6 g. of pure tris(trimethylsilyl)methylsilane, b.p. 96-100°/7 mm., m.p. 57-59° (lit. value (79) b.p. 94-99°/7 mm., m.p. 57-59°). Redistillation of the impure fraction afforded 40.5 g. of pure tris(trimethylsilyl)methylsilane. The total yield was 46.8%.

The undistilled solid residue was taken up in 95% ethanol and filtered to give 81.5 g. of product, m.p. 114-126°. Several recrystallizations from ethanol and finally from ethanol-ethyl acetate (9:1), gave 52.1 g. (19.5%) of pure sym-tetrakis(trimethylsilyl)dimethyldisilane, m.p. 147-148°.

Anal. Calcd. for $C_{14}H_{42}Si_6$: Si, 44.5; mol. wt., 379. Found: Si, 43.9, 44.2; mol. wt., 385, 383.

The infrared spectrum (CCl_4) showed pertient peaks at (μ) 3.40(m), 3.45(m), 7.79(shoulder)(s), 8.06(s). The region below 10 μ (in CS_2) showed peaks at 12.0(s), 12.8(s), 13.1(s) and 14.6(w). The ultraviolet spectrum did not show any absorption above 210 mμ.

Run 2. The reaction was initiated by adding a solution (25 ml.) of 7.48 g. (9.5 mole) of methyltrichlorosilane in 100 ml. of THF to a rapidly stirred mixture of 140 g. (1.3 moles) of chlorotrimethylsilane, 23.1 g. (3.3 g.-atoms) of lithium and 100 ml. of THF. After 5 min., the remainder of the solution was added dropwise over 2.5 hours. The contents of the flask was maintained at ca. 20° for the first 5 hours. After 24 hours of stirring, the reaction mixture was filtered from the excess lithium, hydrolyzed with dilute hydrochloric acid and worked up in the manner described above. Vacuum distillation gave, in four fractions, 59.5 g. of product that was shown by v.p.c. to contain tris (trimethylsilyl)methylsilane as the major component. This impure

material was chromatographed on neutral alumina and the products eluted by petroleum ether were redistilled to give 47.2 g. (36.0%) of pure tris (trimethylsilyl)methylsilane, b.p. 95-99°/7 mm.

The semi-solid, undistilled residue from the first distillation was taken up in 95% ethanol. Filtration produced an oily solid which after two recrystallizations from ethanol:ethyl acetate (9:1) afforded 30 g. (16.1%) of sym-tetrakis(trimethylsilyl)dimethyldisilane, m.p. 145-148° 145-148° (mixed m.p.).

Run 3. A solution (50 ml.) of 41 g. (0.26 mole) of methyltrichlorosilane in 200 ml. of THF was added to a mixture of 14.0 g. (2.0 g.-atoms) of lithium, 136 g. (1.5 moles) of chlorotrimethylsilane and 200 ml. of THF. An exothermic reaction started after the mixture was stirred rapidly for ca. 1.5 hr. The remainder of the solution was then added dropwise during 4 hours. After 12 hours the mixture was filtered from the excess lithium, hydrolyzed and worked up as usual. Distillation gave a total of 28 g. (41.2%) of tris(trimethylsilyl)methylsilane. The undistilled residue was taken up in petroleum ether and chromagraphed on basic alumina. Elution with the same solvent gave an oil from which was isolated 17.6 g. (18%) of sym-tetrakis(trimethylsilyl)dimethyldisilane, m.p. 146-148°.

Three additional runs gave tris(trimethylsilyl)methylsilane in 38-42% yield and sym-tetrakis(trimethylsilyl)dimethyldisilane in 15-20% yield.

Octamethyltrisilane

Run 1. To a rapidly stirred mixture of 21 g. (3.0 g.-atoms) of lithium, 180 g. (1.66 moles) of chlorotrimethylsilane and 250 ml. of THF was added to a solution (25 ml.) of 65 g. (0.5 mole) of dichlorodimethylsilane in 200 ml. of THF. After ca. 4 min., an exothermic reaction started and the remainder of the solution was added dropwise during 8 hrs. Subsequent to an additional 14 hours of stirring, the solution was decanted from the insoluble salts and excess lithium. Most of the solvent and excess chlorotrimethylsilane were then removed by simple distillation. The residue was taken up in petroleum ether, the precipitated lithium chloride was filtered and the solvent was removed. Distillation afforded 52.3 g. of pure octamethyltrisilane, b.p. 68-70°/20 mm., n_D^{20} 1.4611 (lit. value (36) b.p. 175-176°, n_D^{20} 1.4610), and 14.9 g. of the same product containing a small amount of decamethyltetrasilane. The total yield was ca. 65%. Comparison of v.p.c. retention times showed that the undistilled residue contained the corresponding tetra- and pentasilanes. Vapor phase chromatography also indicated that hexamethyldisilane was a product of the reaction.

Run 2. A reaction was initiated in 10 min. by adding 20 ml. of a solution of 65 g. (0.5 mole) of dichlorodimethylsilane to a rapidly stirred mixture of 21 g. (3.0 g.-atoms) of lithium, 180 g. (1.66 moles) of chlorotrimethylsilane and 200 ml. of THF. The remainder of the solution was then added during 12 hours. Subsequent to a work-up similar to that described above, fractional distillation gave 70.3 g. (69%) of octamethyltrisilane, b.p. 68-71°/20 mm., n_D^{20} 1.4614. The analagous tetra- and pentasilanes were shown (v.p.c.) to be present in the residue.

Run 3. A solution (20 ml.) of 52 g. (0.4 mole) of dichlorodimethylsilane in 175 ml. of THF was added to a rapidly stirred mixture of 180 g. (1.66 moles) of chlorotrimethylsilane, 21 g. (3.0 g.-atoms) of lithium and 200 ml. of THF. After 20 min. of stirring the dichlorosilane in THF was added dropwise during 9 hours. The reaction was continued for 18 hours and worked up as described above. Fractional distillation produced 51.5 g. (61.3%) of octamethyltrisilane, b.p. 79-83°/30 mm., n_D^{20} 1.4613.

2-Ethylheptamethyltrisilane

A solution (25 ml.) of 28.2 g. (0.2 mole) of methylethyldichlorosilane in 175 ml. of THF was added to a mixture of 7.0 g. (1.0 g.-atom) of lithium, 86.5 g. (0.8 mole) of chlorotrimethylsilane and 100 ml. of THF. An exothermic reaction started after 5 min. of rapid stirring and the remainder of the solution was added during 12 hours. Subsequent to a total of 24 hours of stirring the reaction mixture was filtered from the excess lithium and the volatiles were removed on a rotary evaporator. The residue was taken up in ether, hydrolyzed with dilute acid, and worked up as usual. After the organic solvents were removed, the crude product was distilled to give 32 g. (65.6%) of 2-ethylheptamethylsilane, b.p. 67-69/5 mm., n_D^{20} 1.4710, d^{20} 0.7960.

Anal. Calcd. for $C_9H_{26}Si_3$: mol. wt., 208.6; MR_D 76.93. Found: mol. wt., 207.3, 206.5; MR_D 76.70.

The infrared spectrum (cap cell) showed bands at the folling positions (μ): 3.36(s), 3.45(s), 8.02(s), 9.90(m), 10.94(w), 11.6-12.0(s), 12.75-12.90(s), 13.5(m). The ultraviolet spectrum consisted of a λ_{max} at 215 mμ .

Continued distillation produced mixtures (5 g.) containing two products that were probably the corresponding tetra- and pentasilanes. The infrared spectrum of the mixture showed the same absorptions as 2-ethylheptamethyltrisilane.

Tris(trimethylsilyl)phenylsilane from phenyltrichlorosilane, lithium and chlorotrimethylsilane in THF

A solution (10 ml.) of 21.5 g. (0.11 mole) of phenyltrichlorosilane in 75 ml. of THF was added to a mixture of 4.4 g. (0.63 g.-atom) of lithium, 54 g. (0.5 mole) of chlorotrimethylsilane and 100 ml. of THF. After 5 min. of stirring, an exothermic reaction began and the remainder of the solution was added during 3 hours. All of the lithium was consumed after stirring overnight(ca. 15 hrs.). The mixture was hydrolyzed, the orgainc layers were separated and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure and 95% ethanol was added to the residue to cause immediate precipitation of a product. The crystals were filtered and washed with ethanol to give 17.6 g. of impure material, m.p. 201-210°. Recrystallization from benzene-ethyl acetate afforded 14.6 g. (23.6%) of tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane, m.p. 216-223°. A mixed melting point with a previously prepared sample[1] was not depressed.

The residue from the original mother liquor was chromatographed on neutral alumina. Elution with petroleum ether gave a liquid that

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[1]A sample was kindly supplied by C. L. Smith, Iowa State University of Science and Technology, Ames, Iowa.

afforded, upon distillation, 3.9 g. (12.3%) of tris(trimethylsilyl) phenylsilane, b.p. (sublimes) ca. 100 to 110°/0.03 mm. (lit. value (19) sublimes at 140°/0.05 mm). The product was identified by its v.p.c. retention time and infrared spectrum.

Tris(trimethylsilyl)phenylsilane from phenyltrichlorosilane, lithium and chlorotrimethylsilane in THF-ether

Run 1. To a flask containing 8.0 g. (1.1 g.-atoms) of lithium, 86.8 g. (0.8 mole) of chlorotrimethylsilane in 100 ml. of ether was added 3.0 g. (0.014 mole) of phenyltrichlorosilane. After 20 min. of rapid stirring there was no evidence that a reaction had started. One-hundred milliliters of ether:THF (1:1) were added, and after another 5 min. of stirring an exothermic reaction began. A solution of 21.1 g. (0.1 mole) of phenyltrichlorosilane in 100 ml. of ether was then added during 10 hours. After 17 hours of stirring v.p.c. showed the presence of the expected product as the major component, and small amounts of higher boiling compounds. Subsequent to removal of the solvents, the residue was taken up in ether and hydrolyzed with dilute acid. The organic layers were separated, dried over anhydrous sodium sulfate and the solvent was removed on a rotary evaporator. Distillation of the residue produced 7.5 g. of forerun, b.p. 70-95°/0.03 mm., containing ca. 3 g. of the expected product. Continued distillation afforded 17 g. of pure tris(trimethylsilyl)phenylsilane. The total yield was ca. 56%.

The undistilled residue was dissolved in ethyl acetate and upon standing there crystallized 1.5 g. of impure material, m.p. 200-211°. Recrystallization from ethyl acetate gave 1.2 g. of tris(trimethylsilyl)

(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane, m.p. and mixed melting point 222-226°.

Run 2. To 5.0 g. (0.71 g.-atom) of lithium, 43.6 g. (0.4 mole) of chlorotrimethylsilane, 80 ml. of ether and 20 ml. of THF was added a solution (5 ml.) of 21.1 g. (0.1 mole) of phenyltrichlorosilane in 125 ml. of ether:THF (4:1). No change was observed after 15 min. of rapid stirring. Subsequent to the addition of six drops of 1,2-dibromoethane and 15 ml. of THF, stirring was continued and an exothermic reaction started in 30 minutes. There was then added 50 ml. of ether followed by the dropwise addition of the trichlorosilane-THF solution during 8 hours. Subsequent to a work-up similar to that described above, the products were distilled to give 17.2 g. (52.6%) of tris trimethylsilyl)phenylsilane containing about 1% impurities.

The undistilled residue was dissolved in hot ethanol and upon standing there crystallized 0.5 g. of impure tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane, m.p. 212-221°. Recrystallization from ethyl acetate raised the melting point to 219-224° (mixed m.p.).

Run 3. To a mixture of 100 ml. of ether, 30 ml. of THF, 93 g. (0.88 mole) of chlorotrimethylsilane and 9.8 g. (1.4 g.-atoms) of lithium was added to a solution (5 ml.) of 47.0 g. (0.22 mole) of phenyltrichlorosilane in 100 ml. of ether. An exothermic reaction started after ca. 5 min. of rapid stirring and there was added another 50 ml. of ether. The remainder of the solution containing the trichlorosilane was added dropwise during ca. 12 hours. After 25 hours the reaction was stopped and the mixture was filtered from the excess lithium.

The volatiles were removed on a rotary evaporator; the residue was taken up in ether and hydrolyzed with dilute acid. Removal of the solvent from the dried organic layer and distillation gave 36.0 g. (50.5%) of tris(trimethylsilyl)phenylsilane. V.p.c. indicated that the undistilled residue contained a small amount of tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane which was not isolated.

Tris(trimethylsilyl)phenylsilane form phenyltrichlorosilane, magnesium and chlorotrimethylsilane

To a flask containing 9.6 g. (0.4 g.-atom) of magnesium, 2.1 g. (0.01 mole) of phenyltrichlorosilane and 20 ml. of THF was added 10 drops of ethyl iodide. Upon stirring an exothermic reaction started, and after 3 min., 10.8 g. (0.1 mole) of chlorotrimethylsilane was added. This was followed by the dropwise addition of a solution of 13.0 g. (0.06 mole) of phenyltrichlorosilane in 75 ml. of THF during 3 hours. The reaction was continued for 2 days and the mixture was filtered from the excess magnesium, hydrolyzed with dilute acid and worked up as usual. The solvents and other volatiles were removed under reduced pressure. Distillation of the residue afforded 4.2 g. (25.5%) of tris(trimethylsilyl)phenylsilane containing ca. 2% impurities, b.p. (sublimes) ca. 135-140°/0.03 mm. Distillation was continued to give a second sublimable solid (ca. 165°) which solidified in the side-arm of the apparatus. Two recrystallizations from 98% ethanol gave 0.9 (2.9%) of sym-tetrakis(trimethylsilyl)diphenyldisilane, m.p. (sealed tube) 374-378°.

Anal. Calcd. for $C_{24}H_{46}Si_4$: mol. wt., 449. Found: mol. wt. 441, 443. The infrared spectrum (CCl_4) showed pertinent peaks at (μ) 3.6 (w), 3.40(w), 3.45(m), 7.0(m), 8.09(s), 8.42(w), 9.25(m). The n.m.r. spectrum consisted of a multiplet for the phenyl protons at 2.69 and a singlet for the methyl protons at 8.75 . The ratio of protons (Ph: CH_3) was 1:3.6 (calcd. 1:3.6). The ultraviolet spectrum showed a shoulder at 235 mμ.

2-Phenylheptamethyltrisilane.

Run 1 (THF). To a flask containing 3.5 g. (0.5 g.-atom) of finely cut lithium wire in 75 ml. of THF was added a solution of 54.3 g. (0.5 mole) of chlorotrimethylsilane and 1.0 g. of methylphenyldichlorosilane in 50 ml. of THF. An exothermic reaction started after ca. 10 min. of rapid stirring. There was then added dropwise a solution of 38.2 g. (0.2 mole) of the dichlorosilane in 100 ml. of THF during 4 hours. Subsequent to stirring for a total of 18 hours, the excess lithium and salts were removed by filtration. The filtrate was then hydrolyzed and the organic layers were separated, combined and dried over anhydrous sodium sulfate. The solvents were removed and the oily residue was distilled to give 18.3 g. (25.1%) of 2-phenylheptamethyltrisilane, b.p. 106-108/3.0 mm., n_D^{20} 1.5233 (lit. value (30) b.p. 133/19 mm., n_D^{20} 1.5236). The undistilled residue was chromatographed on neutral alumina and eluted with petroleum ether to give an oil which began to crystallize after standing for several days. A mixture of ethyl acetate and methanol was then added and trituration induced further crystallization. Filtration afforded 5.7 g. of product, m.p. 99-110°. Two recrystallizations from ethyl acetate-methanol gave 5.6 g. (5.0%)

of pure bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane, m.p. 120-121°.

Anal. Calcd. for $C_{25}H_{62}Si_7$: Si, 35.17; mol. wt., 559.3. Found: Si, 35.0, 34.7; mol. wt., 562.

Run 2 (ether-THF). A solution (10 ml.) of 96 g. (0.5 mole) of methylphenyldichlorosilane in 300 ml. of ether was added to a mixture of 120 g. (1.13 moles) of chlorotrimethylsilane, 18.0 g. (2.5 g.-atoms) of lithium, 100 ml. of ether and 30 ml. of THF. An exothermic reaction began after 5 min. of rapid stirring and there was then added an additional 50 ml. of ether. The remainder of the solution was added during 20 hours. Stirring was continued for a total of 30 hours and the reaction mixture was worked up as described above. Distillation of the crude products gave 73 g. (54.5%) of 2-phenylheptamethyltrisilane, b.p. 135-137°/20 mm., n_D^{20} 1.5238. Although no other products were isolated, v.p.c. showed the presence of a small quantity of the known bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane.

Run 3 (ether-THF). To a rapidly stirred mixture of 4.2 g. (0.6 g.-atom) of lithium, 65 g. (0.6 mole) of chlorotrimethylsilane, 60 ml. of ether and 10 ml. of THF was added a solution (5 ml.) of 19.2 g. (0.1 mole) of methylphenyldichlorosilane in 100 ml. of ether. After 10 min., the remainder of the solution was added during 8 hours. The reaction was continued for 24 hours and worked up as usual to give 13.6 g. (51.0%) of 2-phenylheptamethyltrisilane. V.p.c. showed that the residue contained higher boiling products which were not isolated.

Bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane

From methylphenyldichlorosilane, lithium and chlorotrimethylsilane

Run 1. To a rapidly stirred mixture of 7.0 g. (1.0 g.-atom) of lithium, 47.2 g. (0.39 mole) of chlorotrimethylsilane and 75 ml. of THF was added 2.0 g. (0.01 mole) of methylphenyldichlorosilane. An exothermic reaction began almost immediately and after 10 min. of stirring another 0.39 mole of chlorotrimethylsilane in 50 ml. of THF. This was followed by the dropwise addition of a solution of 17.1 g. (0.09 mole) of methylphenyldichlorosilane in THF. The addition was completed in 5 hours and stirring was continued for a total of 40 hours. The excess lithium and salts were filtered and the volatile components were removed under reduced pressure. Ether was added to the residue and the mixture was hydrolyzed with dilute acid. Subsequent to removal of the solvent, ethyl acetate-methanol (5:1) and a crystal of the expected product were added. Upon standing in a refrigerator overnight, there crystallized 27.2 g. of product, m.p. 114-117°. Concentration of the mother liquor gave an additional 1.5 g. of the impure compound. Recrystallization of the combined fractions, from ethyl acetate-methanol (5:1), afforded 28 g. (50.1%) of pure bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl) cyclohexen-1-yl)methylsilane, m.p. 120-121° (mixed m.p.). No other products were isolated from the oily residue which was shown (v.p.c.) not to contain 2-phenylheptamethyltrisilane. Table 6 gives the infrared data for the cyclohexene.

Table 6. Infrared Spectral Data for Bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane and Related Compounds

Band Position (microns)	Intensity	Characteristic
3.35,3.45	m,m	aliphatic C-H
6.25-6.3	w	C=C
7.20	m	Si-Me
7.9, 8.03	s	Si-Me
8.39, 8.64	w,w	probably SiC=C
8.99, 9.10	w,w	———
10.6, 10.75	w,w	———
12.0, 13.9, 14.6	s,m,w	Si-Me

The n.m.r. spectrum (CCl_4) showed a doublet (J = 5 cps) at 4.12 for the olefinic protons, a series of peaks between 7.83 and 9.0 due to the cyclohexyl protons and two broad, unresolved peaks due to the methyl protons. The ratio of olefinic to cyclohexyl protons was 1:4 (calcd. 1:4). Expansion of the methyl region (50 cps) gave a spectrum showing a peak which was assigned to the single methyl bonded to silicon and five peaks due to the Si-Me groups. The relative areas for the latter protons were ca. 2:1:1:1:1. The ultraviolet spectrum consisted of a peak (λ_{max}) at 241 mμ.

Run 2. The reaction was initiated by adding a solution (30 ml.) of 9.58 g. (0.05 mole) of methylphenyldichlorosilane in 70 ml. of THF

to a rapidly stirred mixture of 41.8 g. (0.6 g.-atom) of lithium, 65.1 g. (0.6 mole) of chlorotrimethylsilane and 100 ml. of THF. After 10 min., the remainder of the solution was added during 5 hours. Subsequent to 6 hours of stirring at room temperature, the mixture was heated ca. 55° for 18 hours. The usual work-up afforded 19.0 g. (67.9%) of the expected product, m.p. and mixed m.p. 120-121°. V.p.c. showed that 2-phenylheptamethyltrisilane was not a final product of the reaction.

Run 3. The reaction was run at room temperature for 28 hours using the quantity of materials given in Run 2. A purification procedure similar to that described in Run 1 gave 18.5 g. (66.4%) of the expected product, m.p. 119.5-121° (mixed m.p.). No other known products were detected by v.p.c.

From 2-phenylheptamethyltrisilane

A mixture of 1.0 g. (0.14 g.-atom) of lithium, 54 g. (0.02 mole) of 2-phenylheptamethyltrisilane, 10.8 g. (0.1 mole) of chlorotrimethylsilane and 30 ml. of THF was stirred at room temperature for 40 hours. The reaction mixture was then hydrolyzed with acid and worked up in the usual manner. Removal of the organic solvents left a residue that was taken up in ethyl acetate-methanol and seeded with a crystal of the expected product. Upon standing there crystallized 1.3 g. of product, m.p. 105-115°. Recrystallization gave 1.1 g. (16.5%, based on the unrecovered starting material) of pure bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane, m.p. 120-121° (mixed m.p.). Removal of the solvents from the mother liquor and distillation gave 2.1 g. (38.9%) of recovered 2-phenylheptamethyl-

trisilane. No other products were isolated from the oily residue.

From tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane

A solution of 5.6 g. (0.009 mole) of the polysilane and 2.0 g. of iodine in 75 ml. of dry benzene was refluxed gently for 20 hours. At the end of this time most of the iodine had reacted and another 0.5 g. of the halogen was added. Stirring at reflux temperature, was continued for an additional 5 hours. The solution was allowed to cool to room temperature, and there was then added 50 ml. of ether and an excess of freshly prepared methylmagnesium iodide. Subsequent to 5 hours of refluxing, the reaction mixture was hydrolyzed with acidified ice and the organic layers were separated and dried over anhydrous sodium sulfate. The solvents were removed and a crystal of the expected compound, and ethyl acetate-methanol was added to the residue. Upon standing, there crystallized 2.3 g. of material, m.p. 175-190°. V.p.c. indicated that the expected product and the starting compound were the components of the mixture. The mother liquor also contained more of the two compounds. Attempted fractional crystallization, in most cases, produced mixtures with melting points between those of the two compounds. A fraction (m.p.121-124°) was finally isolated which contained only a trace of the starting compound. A mixed melting point with an authentic sample of the expected product was not depresses. The structure of the product was further confirmed by its ultraviolet (λ max 242 mμ) and infrared spectra.

A mixture of authentic samples of the two compounds melted over the range 185-200° while the melting points of the pure product and

starting material were 119.5 and 217-220°, respectively.

Tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane

From phenyltrichlorosilane, lithium and chlorotrimethylsilane.

Preparations were carried out under a variety of conditions designed to determine the effect of the following on the yield of product: ratio of reactants, sodium-content of the lithium, reaction temperature, speed of stirring and reaction time. The results of these reactions are given in Table 7 and a representative run is described.

To a rapidly stirred mixture of 5.0 g. (0.715 g.-atom) of finely cut lithium wire (containing ca. 0.8% sodium), 85.6 g. (0.84 mole) of chlorotrimethylsilane and 150 ml. of THF was added a solution (10 ml.) of 11.0 g. (0.052 mole) of phenyltrichlorosilane in 75 ml. of THF. An exothermic reaction started almost immediately and after 5 min., the remainder of the solution containing the trichlorosilane was added dropwise during 6 hours. After 22 hours of stirring, v.p.c. showed the presence of hexamethyldisilane and the absence of tris(trimethylsilyl)phenylsilane. The reaction mixture was then filtered from the excess lithium and the volatiles were removed on a rotary evaporator. The residue was taken up in ether and hydrolyzed with dilute acid. Subsequent to the usual work-up the solvent was removed on a rotary evaporator and a mixture of ethyl acetate-methanol was added to the semi-solid residue to cause immediate precipitation of the product. The mixture was then cooled in an ice bath for 1 hr. and filtered to give 26.7 g. of the expected product, m.p. 222-227°. Concentration of the mother liquor gave a second crop of crystals to bring the total

quantity to 27.8 g. (85.5%). Recrystallization from ethyl acetate or benzene did not alter the melting point.

Anal. Calcd. for $C_{27}H_{68}Si_8$: Si, 36.38; mol.wt., 617.5. Found: Si, 35.9, 36.1; mol. wt., 616 (determined by mass spectrometry). The infrared spectrum gave data consistent with that given in Table 6. The u.v. spectrum showed an absorption (λ max) at 243 mμ (ε= 4,150).

From tris(trimethylsilyl)phenylsilane.

A mixture of 3.4 g. (0.01 mole) of the phenylsilane, 0.9 g. (0.13 g.-atom) of lithium, 8.6 g. (0.08 mole) of chlorotrimethylsilane and 25 ml. of THF was stirred rapidly at 40-50° for 18 hours. The solution was then filtered from the excess lithium and salts and hydrolyzed with dilute acid. The combined organic layers were dried and the volatiles were removed under reduced pressure. A mixture of ethyl acetate and methanol was added to cause immediate precipitation. Subsequent to cooling at 0° for 1 hr., the crystals were filtered to give 2.6 g. of the pure product, m.p. 221-227° (mixed m.p.).

V.p.c. showed that the mother liquor contained only the starting phenylsilane. The solvents were then removed and the dried residue was dissolved in THF. The solution was added to a flask containg more lithium and chlorotrimethylsilane. After 20 hours of stirring, the usual work-up produced another 2.4 g. of the desired compound, m.p. 222-226°. V.p.c. showed that a small quantity of the starting material was still unchanged. The total yield of product was 82.6%. The infrared and ultraviolet spectra of the product were the same as those of an authentic sample.

Table 7. Preparations of Tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane From Phenyltrichlorosilane, Lithium and Chlorotrimethylsilane in THF

Run	Molar ratio Me_3SiCl to $PhSiCl_3$	Molar ratio Lithium[a] to $PhSiCl_3$	Speed of stirring[b]	Temp. (°C)	Time[c] (hrs.)	Yield of product[d]
1	3.3	6.6	Regular	25	19	23.6[e]
2	8.0	11	Rapid	25	17	50.0
3	14	14	Rapid	25	22	75.0
4	14	14	Rapid	25	24	85.5
5	11.6	14	Rapid	25	16	90.0
6	11.6	14	Rapid	55	18	78.0
7	9.8	13	Rapid	55	24	61.5

[a] High sodium-content lithium (0.8% Na), from the Lithium Corporation of America was used unless stated otherwise.

[b] Rapid stirring was obtained with the use of a Hershberg stirrer and an air-driven motor. Regular refers to the speed obtained with a Trubore stirrer.

[c] In all runs, the solution containing the phenylsilane was added during 4 to 5 hours.

[d] A small amount of hexamethyldisilane was formed in all reactions.

[d] A small amount of hexamethyldisilane was formed in all reactions.

[e] Tris(trimethylsilyl)phenylsilane was isolated (12%) from this reaction but was shown (v.p.c.) to be absent in subsequent runs.

Table 7. (continued)

Run	Molar ratio: Me_3SiCl to $PhSiCl_3$	Molar ratio: Lithium[a] to $PhSiCl_3$	Speed of stirring[b]	Temp. (°C)	Time[c] (hrs.)	Yield of product[d]
8	14.0	14	Regular	25	24	70.0
9	14.0	14	Regular	50-60	24	86.0
10	12	14[f]	Rapid	25	15	85.5
11	12	14	Rapid	25	16	89.5

[f] High purity lithium wire (low sodium content) from the Foote Mineral Company was used.

Tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)-4d-cyclohexen-1-yl)silane.

p-Bromodeuterobenzene (80) was prepared in satisfactory yield by the hydrolysis of p-bromophenyllithium with deuterium oxide (99.5%). The lithium reagent was prepared by the reaction of p-dibromobenzene with n-butyllithium (81). An excess of p-deuterophenylmagnesium bromide was prepared in ether and added to 8.6 g. (0.03 mole) of tris (trimethylsilyl)chlorosilane in 50 ml. of THF. When v.p.c. showed the absence of chlorosilane the reaction mixture was hydrolyzed with acidified ice and worked up as usual. The solvents and other volatiles were removed under reduced pressure and the presence of tris(trimethylsilyl)-p-deuterophenylsilane was detected by v.p.c. Although three products were present, the major component had almost the same retention

time as a sample of the non-deuterated compound.

The impure material was dissolved in 75 ml. of THF and added to a reaction flask containing 21.7 g. (0.2 mole) of chlorotrimethylsilane, 2.1 g. (0.3 g.-atom) of lithium and 25 ml. of THF. After 18 hours of rapid stirring, v.p.c. showed that all of the phenylsilane had reacted. The mixture was then filtered from the excess lithium and the volatiles were removed on a rotary evaporator. The residue was taken up with ether, hydrolyzed and worked up as usual. The organic solvents were removed and 95% ethanol was added to cause immediate precipitation. Filtration gave 3.5 g. of the impure compound, m.p. 185-198°. Recrystallization from ethyl acetate raised the melting point to 218-224°. A mixed m.p. with the non-deuterated compound was not depressed. Also, the v.p.c. retention time, infrared, and ultraviolet spectra of the product were the same as those of the non-deuterated cyclohexene. The n.m.r. data are given in the Discussion section.

Tris(3,4,5,6-tetrakis(trimethylsilyl)-
cyclohexen-1-yl)(trimethylsilyl)silane

From Chlorotriphenylsilane

Run 1. (15:1 molar ratio). To a flask containing 10.5 g. (1.5 g.-atoms) of lithium was added a solution of 128 g. (1.1 moles) of chlorotrimethylsilane and 2.0 g. (0.007 mole) of chlorotriphenylsilane in 125 ml. of THF. After 10 min. of rapid stirring, there was then added a solution of 27.5 g. (0.093) mole of chlorotriphenylsilane in 75 ml. of THF during 4.5 hours. After 12 hours of stirring another 42.8 g. (0.4 mole) of chlorotrimethylsilane were added and stirring

was continued for 24 hours. The reaction mixture was then filtered from the excess lithium and hydrolyzed. Filtration, followed by washing with acetone, gave 7.5 g. (6.2%) of the expected product, m.p. 380-384° dec. Recrystallation from benzene (in which the solubility is very low) or a concentrated solution in cyclohexane did not alter the decomposition range,

Anal. Calcd. for $C_{57}H_{132}Si_{14}$: Si, 32.5 mol. wt., 1212. Found: Si, 32.5, 32.4 mol. wt., 1195, 1220 (in toluene).

The infrared spectrum gave data consistent with that given in Table 6. The n.m.r. spectrum showed a doublet (J = 6 cps) for the olefinic protons at 3.55 , two partially resolved broad peaks at 7.60 and 8.23 for the aliphatic ring protons and a series of peaks due to Si-Me between 9.40 and 9.70 . The ratio of protons was the same as the calculated value. Expansion of the methyl region (50 cps) showed four peaks for the trimethylsilyl groups. The signal from the two trimethylsilyl in the allylic positions was a broad unresolved single peak. Ultraviolet absorption bands (λ_{max}) were exibited at 222 and 243 (shoulder) microns.

The aqueous mixture was worked up as usual and the combined organic layers were dried, the solvents were removed and a mixture of ethyl acetate-ethanol was added to the oily residue. The solution was left standing in a refrigerator overnight and the crystallized material was filtered to give 3.7 g. of product, m.p. 200-220°. Three recrystallizations from benzene-ethyl acetate raised the melting point to 282-285°.

The infrared spectrum of this fraction was the same as that of the higher melting product. The n.m.r. spectrum showed the same absorption for the olefinic and aliphatic ring protons as the higher melting product. However, expansion of the methyl region (50 cps) showed a single peak at 9.75 ($Si-SiMe_3$) and a series of eight peaks from 9.83 to 9.87τ. Intergration of the area under the low field peak (9.75τ) and under the series of peaks gave a ratio of 1:12 (calcd. 1:12). This spectral data indicate that the lower melting fraction contained compounds isomeric to the higher melting product.

Concentration of the original mother liquor gave a polymeric grease-like material which solidified to an amorphous solid, m.p. 106-117°, when treated with methanol. The i.r. spectrum of this substance did not show the presence of a phenyl group and was essentially the same as the spectra of the crystalline products.

Run 2. (17:1 molar ratio). To initiate the reaction, a solution of 54 g. (0.5 mole) of chlorotrimethylsilane and 2.0 g. (0.007 mole) of chlorotriphenylsilane in 70 ml. of THF was added to a suspension of 11.2 g. (1.6 g.-atoms) of lithium in THF. An exothermic reaction started after ca. 2 min. of rapid stirring and there was then added 129 g. (1.18 moles) of chlorotrimethylsilane and 150 ml. of THF. After 10 min., a solution of 27.46 g. (0.093 mole) of chlorotriphenylsilane in 75 ml. of THF was added during 3 hours. After 26 hours of stirring the products were worked up as described in Run 1 to give, in addition to the polymeric oil, 20.1 g. (16.5%) of the expected product, m.p. 385-395° dec. (mixed m.p.), and 8.0 g. of the lower melting fraction, m.p. 282-285° (mixed m.p.).

From 1,1,1-trimethyl-2,2,2-triphenyldisilane

To a rapidly stirred mixture of 54.3 g. (0.5 mole) of chlorotrimethylsilane, 3.5 g. (0.5 g.-atom) of lithium and 75 ml. of THF was added 5 ml. of a solution of 10.0 g. (0.03 mole) of the disilane in 50 ml. of THF. After ca. 3 min. of stirring, the remainder of the solution containing the disilane was added dropwise during 2 hours. After 30 hours v.p.c. indicated that all of the disilane had reacted. The reaction mixture was then filtered from the excess lithium, and the usual work-up gave 4.15 g. (11.4%) of the expected product, m.p. 383-390° dec. (mixed m.p.), and 1.5 g. of the lower melting fraction, m.p. 181-185° (mixed m.p.). No other crystalline products could be isolated from the oily residue.

(3,4,5,6-Tetrakis(trimethylsilyl)cyclohexen-1-yl)trimethylsilane (attempted).

A solution of 15.01 g. (0.1 mole) of phenyltrimethylsilane and 65.0 g. (0.6 mole) of chlorotrimethylsilane in 100 ml. of THF was added to 4.0 g. (0.57 g.-atom) of lithium in 25 ml. THF. An exthermic reaction started after 3-4 min. of rapid stirring. After 14 hours, v.p.c. showed the presence of three major products and the absence of the phenylsilane. The products were then worked up as usual to give 28 g. of viscous liquid. Vacuum distillation gave several fractions boiling between 99-130°/0.013. Each contained three components with close v.p.c. retention times. The i.r. spectrum of the mixture gave data identical ot that listed in Table 6.

Attempted Preparation of Tetrakis(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane From Tetraphenylsilane

A reaction was initiated in about 5 min. by rapidly stirring a mixture of 9.8 g. (0.03 mole) of tetraphenylsilane, 7.0 g. (1.0 g.-atom) of lithium and 109 g. (1.0 mole) of chlorotrimethylsilane and 150 ml. of THF. Stirring was continued for 30 hours and the solution was filtered from the excess lithium and lithium chloride. Subsequent to acid hydrolysis, the organic layers were separated and dried over anhydrous sodium sulfate. Removal of the solvents on a rotary evaporator gave a heavy grease-like material that resisted attempts to induce crystallization. The addition of methanol and agitation caused this substance to solidify to an amorphous solid (39.8 g.) m.p. ca. 150-165° dec. Several recrystallizations from ethanol-ethyl acetate raised the decomposition range to 205-215°. When the melting point block was preheated to 200° and the rate of heating was 2° per minute, the range was 220-230°. Chromatography on neutral alumina had no effect on this value. The infrared spectrum showed strong absorptions for the Si-Me groups (see Table 8) but no bands due to Si-Ph.

Hexakis(trimethylsilyl)disilane

Preparations

General procedure for the purification of hexakis(trimethylsilyl)disilane. Subsequent to hydrolysis of the reaction mixture and the usual work-up, the solvents were removed with the aid of a rotary evaporator and ethanol (95%) was added to cause immediate precipitation of a mixture of tetrakis(trimethylsilyl)silane (XI) and hexakis(trimethylsilyl)disilane. The mixture was usually cooled at 0° before

filtration. Compound XI was removed by fractional sublimation at ca. 75°/0.01 mm. The disappearance of this compound was followed by v.p.c. The residue was usually dissolved in a mixture of hot ethyl acetate-methanol and 2 to 3 recrystallizations were required to give pure hexakis(trimethylsilyl)disilane. Acetone was found to be best the best solvent for recrystallization.

The silyllithium (XIX) was prepared by the reaction of XI with methyllithium in accordance with a reported (25,18,77) procedure. The quantity of uncleaved XI was determined by quantitative v.p.c. estimations, or by hydrolyzing an aliquot of the silyllithium conpound and isolating the unchanged polysilane (XI). The yield of hexakis (trimethylsilyl)disilane was based on the quantity of tetrakis(trimethylsilyl)silane to the silyllithium (XIX).

From tris(trimethylsilyl)silyllithium and 1,2-dibromoethane reverse addition (at 25°). To a solution of the silyllithium prepared from 0.082 mole of tetrakis(trimethylsilyl)silane (XI) was added 7.7 g. (0.041 mole) of 1,2-dibromoethane in 100 ml. of THF. An exothermic reaction began immediately with the appearance of a red-brown color that persisted until only 15 ml. of the solution was left. The addition was stopped at this point and stirring was continued for an additional 2 hours; Color Test I was negative at this time. The mixture was hydrolyzed with dilute acid and the organic layers were separated and dried over sodium sulfate. Subsequent to removal of the solvents, ethanol-methanol was added to cause immediate precipitation. The mixture was cooled in an ice bath for 1 hour and filtered to give 14.5 g. of an oily solid. Concentration of the mother liquor

gave an additional 1.3 g. of product. Fractional sublimation at 75°/0.01 mm. afforded 9.2 g. of XI, m.p. 288-295° (mixed m.p.). When v.p.c. indicated that all of XI had been removed, the residue was dissolved in ethyl acetate-methanol. The solution was cooled at ca. 15° overnight and filtered to give 1.5 g. of product 345-361°. Two recrystallizations from ethyl acetate-methanol gave 1.3 g. (6.5%) of hexakis(trimethylsilyl)disilane, m.p. 371-375° dec.

Anal. Calcd. for $C_{18}H_{54}Si_8$: Si, 45.4; mol. wt., 495.3. Found: Si, 45.1, 45.1, mol. wt. 509.7.

The infrared spectrum was consistent with the assigned structure. The data for this and other permethylated polysilanes are given in Table 8.

Removal of the solvents from the mother liquor gave a heavy oil which was shown (v.p.c.) to contain four products with close retention times. An infrared spectrum of the mixture showed the usual absorption for the $Si-CH_3$ group and a sharp band at 9.3(s) μ. This peak does not appear to be due to the presence of Si-O-Si since this group usually gives rise to a broad absorption band in this area.

Normal addition (at 25°). A solution (250 ml.) of tris(trimethylsilyl)silyllithium, prepared from 0.098 mole of tetrakis(trimethylsilyl)silane (XI), was added to 9.2 g. (0.049 mole) of 1,2-dibromoethane in 75 ml. of THF during 1.5 hours. Color Test I was negative after an additional 30 min. of stirring. The mixture was hydrolyzed with acid and worked up as usual. Ethanol (95%) was added to the residue; the mixture was cooled at 0° for 1 hr. and filtered to give the crude product. Fractional sublimation afforded 9.8 g. of XI, m.p.

Table 8. Infrared-Data for Hexakis(trimethylsilyl)disilane and Other Polysilanes Containing Only the Si-Me Group.[a]

Band Position (microns)	Intensity
3.4, 3.45	m, m
7.2	
7.9-8.05	s
12.0	s
13.5	s
14.6	m

[a] The spectrum of all compounds of this type show essentially the same bands below about 11.0 microns; however, the absorption between 11 and 15 microns depends on the number of methyl groups attached to a given silicon atom (40). The values given here are for hexakis(trimethylsilyl)disilane and tetrakis(trimethylsilyl) silane.

295-300°. Purification of the residue produced 1.8 g. of pure hexakis (trimethylsilyl)disilane, m.p. 374-379° dec. (mixed m.p.).

Reverse addition (at ca. -70°) - Run 1. A solution of 5.2 g. (0.034 mole) of 1,2-dibromoethane in 75 ml. of THF was added, during 1 hr., to a solution of the silyllithium (XIX), prepared from 21.5 g. (0.067 mole) of tetrakis(trimethylsilyl)silane (XI). Throughout the addition the reaction flask was cooled to ca.-70° with the use of a Dry Ice-acetone bath. When the addition was complete, stirring was continued for 30 min. at this low temperature, (Color Test I was negative) and the mixture was hydrolyzed with dilute acid and worked

up in the usual manner. Fractional sublimation of the crude products afforded 1.8 g. of XI (identified by v.p.c.) while purification of the residue gave 8.47 g. (51%) of pure hexakis(trimethylsilyl)disilane, m.p. 373-378° dec. A mixed melting point with a previously prepared sample was not depressed.

Run 2. Tris(trimethylsilyl)silyllithium (XIX) was prepared from 9.6 g. (0.03 mole) of tetrakis(trimethylsilyl)silane (XI). To the solution of XIX at -70° was added 2.82 g. (0.015 mole) of 1,2-dibromoethane in 50 ml. of THF. The addition was complete in 45 min. and stirring was continued for another 30 min. The reaction mixture was hydrolyzed and worked up as decribed above. The usual purification procedure gave 1.2 g. of XI and 3.34 g. (45%) of the expected product, m.p. 374-380° dec.

Run 3. To a solution of the silyllithium (XIX) prepared from 10.0 g. (0.03 mole) of XI was added, a solution of 3.0 g. (0.016 mole) of 1,2-dibromoethane in 50 ml. of THF during 40 min. The reaction flask was cooled to ca. -70° through the addition. After a total of 1.5 hr. the mixture was hydrolyzed and the products were worked up as usual. The organic solvents were removed and 95% ethanol was added to the residue to cause immediate precipitation of 3.6 g. of product, m.p. 220-232°. Concentration of the mother liquor gave an oily residue from which no solid products were isolated. The impure solid material was subjected to sublimation to remove a small amount (ca. 0.15 g.) of tetrakis(trimethylsilyl)silane. The residue, subsequent to two recrystallizations from acetone, gave 3.3 g. (43.5%) of hexakis(trimethylsilyl)disilane, m.p. 374-379°.

From tris(trimethylsilyl)silyllithium (XIX) and iodine reverse addition (25°). A solution of 7.6 g. (0.03 mole) of iodine in 150 ml. of THF was added dropwise to a solution of XIX, prepared from 0.082 mole of tetrakis(trimethylsilyl)silane (XI). An exothermic reaction was observed as the color of the halogen disappeared immediately upon addition. The solution was added in 3 hours an stirring was continued overnight. The mixture was then hydrolyzed with dilute acid, the organic layers were separated and dried over anhydrous sodium sulfate. The volatiles were removed under reduced pressure and ethanol was added to cause immediate precipitation of 15.1 g. of product, m.p. 175-200°. Fractional sublimation at 80°/0.01 mm. gave 9.9 g. of XI, m.p. 298-310° (mixed m.p.). The sublimation residue was dissolved in ethyl acetate to which methanol was added. Upon standing, there crystallized 2.0 g. of product, m.p. 340-355°. Two recrystallizations from the same solvent mixture gave 1.8 g. of hexakis(trimethylsilyl) disilane, m.p. 372-377° dec. (mixed m.p.).

Removal of the solvents from the original mother liquor gave a heavy oil containing two of the same unidentified products that were present in the residue from the reaction of the lilyllithium (XIX) with 1,2-dibromoethane.

Normal addition (25°). A solution of tris(trimethylsilyl) silyllithium, prepared from 21.5 g. (0.067 mole) of XI, was added to a solution of 4.3 g. (0.017 mole) of iodine in 75 ml. of THF. Color Test I was positive after ca. 50% of the solution had been added. An additional 4.3 g. of iodine were added and the addition of the silyllithium was completed in 30 minutes. Subsequent to an additional 15

min. of stirring the reaction mixture was hydrolyzed and worked up as usual. The purification procedure described gave 10.2 g. of XI and 1.2 g. (8.3%) of hexakis(trimethylsilyl)disilane, m.p. 372-378° dec.

Reverse addition (-70°). Tris(trimethylsilyl)silyllithium (XIX) was prepared from 19.3 g. (0.06 mole) of tetrakis(trimethylsilyl) silane (XI). The solution of XIX was cooled to ca. -70° and a total of 4.3 g. (0.028 mole) of iodine in THF was added during 45 minutes. Color Test I was negative immediately after the addition was completed, however, stirring was continued for an additional 30 min. The reaction mixture was hydrolyzed and worked up as usual. The solvents were removed from the combined organic layers and ethanol was added to the residue. Subsequent to cooling in a Dry Ice-acetone bath, filtration afforded 4.5 g. of the crude product mixture. The usual purification procedure gave 1.1 g. of XI, m.p. 313-318° and 2.9 g. (19.5%) of hexakis(trimethylsilyl)disilane, m.p. 374-379° dec. Removal of the solvents from the mother liquor gave an oily residue which, after chromatography on basic alumina, did not yield any additional solid products. Other than the usual absorption bands for Si-Me, the i.r. spectrum of the residue showed a weak band at ca. 9.5 micron.

From tris(trimethylsilyl)silyllithium (XIX) and mercury (II) chloride. To a flask containing 10.85 g. (0.04 mole) of the chloride in 75 ml. of THF was added a solution of XIX prepared from 0.082 mole of XI. An exothermic reaction began immediately, and the mixture acquired a black color. The solution was added over a 2 hr. period and stirring was continued for another 3 hours. Filtration

of the mixture gave 7.3 g. of mercury. Hydrolysis and the usual work-up followed. The organic solvents were removed and the residue, after addition of ethanol, was cooled in a Dry Ice-acetone bath. Filtration gave 12 g. of the crude mixture containing tetrakis(trimethylsilyl) silane (XI) and hexakis(trimethylsilyl)disilane. Fractional sublimation afforded 9.3 g. of compound XI, m.p. 288-297° (mixed m.p.). The residue, subsequent to 3 recrystallizations from ethyl acetate-methanol, gave 1.2 g. (5.3%) of hexakis(trimethylsilyl)disilane, m.p. 373-378° dec. (mixed m.p.).

A second run was made using twice the quantities given above. The mecuric chloride was added to the silyllithium, and a purification procedure similar to that described in the first run was used. This reaction gave 17.5 g. of XI and 2.1 g. (4.7%) of hexakis(trimethyl-silyl)disilane.

From tris(trimethylsilyl)chlorosilane and tris(trimethylsilyl) silyllithium (XIX), (Run 1. 25°). To a solution of 20.4 g. (0.073 mole) of the chlorosilane in 100 ml. of THF was added a solution of the silyllithium XIX prepared from 0.07 mole of tetrakis(trimethyl-silyl)silane. The addition was completed in 1 hr. and stirring was continued for an additional 1.5 hours. The reaction mixture was then hydrolyzed with dilute acid and worked up in the usual manner. The organic solvents were removed under reduced pressure and ethanol was added. Subsequent to cooling for 1 hr. in an ice bath, filtration gave 21.1 g. of the crude mixture, m.p. 165-195°. The usual subli-mation procedure produced 17.4 g. of XI, m.p. 292-300° (mixed m.p.). The residue afforded, subsequent to 3 recrystallizations from ethyl

acetate-methanol, 2.3 g. (6.4%) of hexakis(trimethylsilyl)disilane, m.p. 373-377 ° dec. (mixed m.p.).

Run 2 (-70°). A solution of the silyllithium (0.08 mole) was added dropwise to 20.4 g. (0.073 mole) of the chlorosilane in 75 ml. of THF. The reaction temperature was maintained at ca. -70° during the 1.5 hr. required for the addition. After a total of 2 hours, the mixture was hydrolyzed by addition of dilute acid. A work-up similar to that described above produced 2.7 g. of tetrakis(trimethylsilyl) silane and 4.6 g. (25%) of hexakis(trimethylsilyl)disilane.

From tris(trimethylsilyl)chlorosilane and magnesium. A mixture of 12.4 g. (0.1 g.-atom) of magnesium, 13.8 g. (0.05 mole) of the chlorosilane, 8 drops of ethyl iodide and 75 ml. of THF was refluxed for 4 hours. After this time, there was no evidence that a reaction had started. However, upon standing overnight, the solution acquired a red-brown color. Stirring, at reflux temperature, was then continued for 6 hours. The mixture was then cooled, filtered from the insolubles and hydrolyzed. After the usual work-up the organic solvents were removed. Ethanol was added to the residue which was then cooled at 0° for 1 hour. Filtration gave a mixture of tetrakis(trimethylsilyl) silane (XI) and hexakis(trimethylsilyl)disilane. Purification of a fraction of the mixture gave 1.0 g. of XI, m.p. 292-300° (mixed m.p.) and 0.43 g. of the hexakis(trimethylsilyl)disilane m.p. 368-372° dec. (mixed m.p.). The reaction could not be initiated when a repeat run was attempted.

From tris(trimethylsilyl)chlorosilane and sodium (attempted). A mixture of 4.6 g. (0.2 g.-atom) of sodium, 2 ml. of ethyl acetate

and 100 ml. of dry toluene was refluxed until the sodium became molten. There was then added, during 7 hr., a solution of 13.0 g. (0.046 mole) of the chlorosilane and 5 ml. of ethyl-acetate in 75 ml. of toluene. A green color appeared after ca. 1.5 hr. Stirring and refluxing were continued for a total of 24 hours; the mixture was cooled to 0° and ethanol was added to destroy the excess sodium. Acidification and the usual work-up followed. Removal of the organic solvents left an oily residue which was chromatographed on basic alumina. Petroleum ether eluted a mixture that was shown (v.p.c.) to contain tris(trimethylsilyl)silane (XVII), three unidentified products and tetrakis(trimethylsilyl)silane. Upon standing a fraction of the latter product crystallized from the solution. A mixed melting point with an authentic sample was not depressed. The i.r. spectrum of the mixture showed, in addition to the usual bands for Si-Me (Table 8), a peak at 4.87 due to the Si-H absorption of XVII.

From hexachlorodisilane, lithium and chlorotrimethylsilane (attempted). The reaction was initiated in ca. 5 min. by adding a solution (10 ml.) of 26.9 g. (0.01 mole) of hexachlorodisilane, in 200 ml. of THF, to a rapidly stirred mixture of 14.0 g. (2.0 g.-atoms) of lithium, 109 g. (1.0 mole) of chlorotrimethylsilane and 200 ml. of THF. The remainder of the solution was added during 6 hours and stirring was continued for 48 hours. The solution was then filtered from the insolubles and hydrolyzed with cold hydrochloric acid. The organic layers were separated and the solvents were removed by steam distillation. Subsequent to the addition of methanol, the mixture was filtered to give 19g. of crude tetrakis(trimethylsilyl)silane (XI). Sublimation produced

17.2 g. (26.6%) of XI, m.p. 290-298° (mixed m.p.). The residue from the mother liquor was chromatographed on neutral alumina. Elution with petroleum ether gave an additional 1.5 g. of XI, and a heavy oil which was shown (v.p.c.) to contain a small amount of XI, but no hexakis(trimethylsilyl)disilane.

From tetrachlorosilane, lithium and chlorotrimethylsilane (attempted). A solution (25 ml.) of 35.6 g. (0.21 mole) of tetrachlorosilane and 3 ml. of ethyl acetate in 100 ml. of THF was added to a mixture of 94.2 g. (0.87 mole) of chlorotrimethylsilane, 15.1 g. (2.2 g.-atoms) of lithium, 3 ml. of ethyl acetate and 150 ml. of THF. An exothermic reaction began after 30 min. and the remainder of the solution was then added during 3 hours. The reaction temperature was maintained at ca. 40° during the first five hours. After 20 hours of stirring, the mixture was filtered, the filtrate was hydrolyzed and worked up as usual. The organic solvents were removed and 95% ethanol was added to cause immediate precipitation of the crude product. Sublimation gave 26.9 g. (40.1%) of tetrakis(trimethylsilyl)silane, m.p. 300-310°. The presence of hexakis(trimethylsilyl)disilane was not detected by v.p.c.

Reactions

With methyllithium. A solution of methyllithium (0.01 mole) was prepared in ether in accordance with a published procedure (82) and was added to 0.5 g. (0.001 Mole) of hexakis(trimethylsilyl)disilane in 10 ml. of THF. The solution acquired a yellow color and after 4 hours an aliquot was removed and hydrolyzed for analysis. In addition

to the starting material, v.p.c. showed the presence of tris(trimethylsilyl)silane and tris(trimethylsilyl)methylsilane. There was no unchanged starting material after stirring overnight.

An attempt to carry out this reaction in ether instead of ether-THF was unsuccessful.

With tris(trimethylsilyl)silyllithium followed by treatment with trimethyl phosphate. A solution of 0.004 mole of the silyllithium and 0.5 g. (0.001 mole) of hexakis(trimethylsilyl)disilane in 10 ml. of THF was stirred for 1.5 hr. and an aliquot was removed and hydrolyzed for analysis by v.p.c. Tris(trimethylsilyl)silane, tetrakis(trimethylsilyl)silane, two unidentified products and unchanged hexakis- were detected. After 12 hours of stirring the reaction mixture was derivatized with trimethyl phosphate, and hydrolyzed with dilute acid. The organic layer was analyzed by v.p.c., and the following were shown to be present: tris(trimethylsilyl)methylsilane, tetrakis(trimethylsilyl)silane, sym-tetrakis(trimethylsilyl)dimethyldisilane and a small amount of a product that was probably the unknown pentakis(trimethylsilyl)methyldisilane.

With triphenylsilyllithium. A solution of 0.5 g. (0.001 mole) of hexakis(trimethylsilyl)disilane in 10 ml. of THF was added dropwise to 0.1 mole of triphenylsilyllithium prepared in THF. The reaction mixture was stirred for 10 min. and an aliquot was hydrolyzed for analysis. The following known products were shown (v.p.c.) to be present: triphenylsilane, 1,1,1-trimethyl-2,2,2-triphenyldisilane and unchanged starting material. In addition, there was a product, the retention time of which indicated that it resulted from the cleavage of a tri-

methylsilyl group from adjacent silicon atoms. After 3 hours of stirring there was no unchanged starting material. The mixture was then hydrolyzed and the organic layers were dried over anhydrous sodium sulfate. The solvents were removed and an infrared spectrum of the residue was taken. In addition to the expected bands for the Si-Me group (see Table 8), a peak was present at 4.78 microns due to an Si-H group.

With lithium. One milliliter of THF was added to a mixture of 1.0 g. (0.002 mole) of hexakis(trimethylsilyl)disilane and 0.7 g. (0.1 g.-atom) of finely cut lithium wire. After ca. 5 min. of stirring a yellow color appeared, indicating that a reaction had started. There was then added dropwise, another 5 ml. of THF. After 1.5 hours of stirring, analysis (v.p.c.) of a hydrolyzed aliquot showed the presence of tris(trimethylsilyl)silane as the major product. Tetrakis(trimethylsilyl)silane and two unidentified products were also present.

With bromine, followed by treatment with methylmagnesium iodide. A solution of 3.2 g. (0.02 mole) of bromine in 15 ml. of dry benzene was added to 1.8 g. (0.004 mole) of heakis(trimethylsilyl)disilane in 25 ml. of benzene. The addition was completed in 30 min., and stirring was continued for an additional 30 min. There was then added 25 ml. of dry THF and an excess of methylmagnesium iodide. This mixture was stirred overnight and was hydrolyzed with acidified ice. Analysis (v.p.c.) of the organic layer showed the presence of sym-tetrakis(trimethylsilyl)dimethyldisilane, a second product that was not identified, and starting material. A partial separation gave 0.7 g. (39%) of unchanged hexakis(trimethylsilyl)disilane.

A solution of 1.0 g. (0.002 mole) of hexakis(trimethylsilyl)disilane in carbon tetrachloride was cooled to -20° and chlorine gas was introduced. After 30 min. of stirring, v.p.c. showed the starting compound to be the only component. The temperature was allowed rise to ca. -10° and the gas was passed through the solution for another 30 minutes. At the end of this time, unchanged hexakis- and two unidentified products were present. The retention times of the latter two indicated that they were compounds resulting from cleavage of peripheral trimethylsilyl groups. The known tris(trimethylsilyl)chlorosilane, which would have resulted from cleavage of the symmetrical Si-Si bond, was not present.

Cleavage on basic alumina (attempted). One gram of hexakis (trimethylsilyl)disilane (m.p. 373-381°) was dissolved in petroleum ether and was left standing on a 3 x 20 cm. column of basic alumina (Matheson, Coleman and Bell, Chromatographic Grade Activated Alumina, 80-200 mesh) for 4.5 hours. Elution with the same solvent and recrystallization from acetone gave 0.85 g. (85%) of recovered hexakis(trimethylsilyl)disilane, m.p. 373-382° (mixed m.p.).

With lithium aluminum hydride (attempted). A mixture of 1.0 g. (0.002 mole) of hexakis(trimethylsilyl)disilane and 1.0 g. (0.03 mole) of lithium aluminum hydride was stirred at room temperature for 18 hours. The only compound that could be detected by v.p.c. was unchanged starting material. The mixture was then refluxed for 3 days with no effect. The mixture was hydrolyzed on ice and worked up as usual to give, subsequent to recrystallization from acetone, 0.85 g. of recovered hexakis (trimethylsilyl)disilane, m.p. 374-379° (mixed m.p.).

Tris(trimethylsilyl)chlorosilane

Preparations

From tris(trimethylsilyl)silane and phosphorus pentachloride. A solution (10 ml.) of 15 g. (0.0606 mole) of tris(trimethylsilyl)silane in 75 ml. of dry petroleum ether (b.p. 60-70°) was added to a mixture of 18.7 g. (0.09 mole) of phosphorus pentachloride and 150 ml. of the same solvent. After 15 min. of stirring, there was no evidence that a reaction had started. The remainder of the solution was added and the mixture was refluxed for 6 hours. At the end of this time, v.p.c. indicated there was no unchanged starting material. The solvent and phosphorus trichloride were removed by simple distillation. Fractionation of the residue afforded 3.4 g. of impure material and 8.5 g. (50%) of pure tris(trimethylsilyl)chlorosilane, b.p. 70-72°/0.5 mm., m.p. 51-52°.

Anal. calcd. for $C_9H_{27}ClSi_4$: Cl, 12.35. Found: Cl, 12.47, 12.54.

The i.r. spectrum showed peaks due only to the Si-Me group (see Table 8). The u.v. spectrum showed a λ_{max} at 250 mμ (ϵ = 4,156).

Vapor phase chromatography indicated that the impure fractions contained another 8 to 10% of the expected chlorosilane. Bis(trimethylsilyl)dichlorosilane was later found to be the major component in the forerun.

A repeat run under similar conditions gave a 49% yield of tris-(trimethylsilyl)chlorosilane.

From tris(trimethylsilyl)silane and carbon tetrachloride (Run 1). Tris(trimethylsilyl)silane, 37.5 g. (0.13 mole), was added to 100 ml. of carbon tetrachloride. An exothermic reaction began immediately.

The excess chloride and chloroform (detected by v.p.c.) were removed at once by distillation at atmospheric pressure. Continued distillation, under reduced pressure gave 7.2 g. of impure forerun and 33.8 g. of pure tris(trimethylsilyl)chlorosilane. Redistillation of the impure material gave another 4.4 g. of the chlorosilane. The total yield of pure product was 89.5%. A mixed melting point with a sample prepared by the phosphorus pentachloride reaction was not depressed.

Run 2. Tris(trimethylsilyl)silane, 24.7 g. (0.1 mole) was added to a distillation apparatus containing 75 ml. of carbon tetrachloride. The excess reagent was removed by distillation and another 75 ml. of the tetrachloride were added. The general distillation procedure was repeated to give 25.7 g. (91%) of pure tris(trimethylsilyl)chlorosilane.

Five repeat runs, using this same general procedure gave 87-92% yields of the chlorosilane.

From tetrakis(trimethylsilyl)silane (XI) and phosphorus pentachloride (attempted). A mixture of 9.6 g. (0.03 mole) of the polysilane (XI) and 6.8 g. (0.033 mole) of phosphorus pentachloride in 100 ml. of carbon tetrachloride was refluxed for 4 hours. V.p.c. analysis showed that a large fraction (ca. 65%) of compound XI was unchanged and that only a small amount of the expected product was present. Analysis at a lower column temperature showed the presence of more volatile components, indicating that more than one trimethylsilyl group was cleaved. Addition of more phosphorus pentachloride caused a further decrease in the quantity of XI; however, no significant amount of tris(trimethylsilyl)chlorosilane could be detected.

From tetrakis(trimethylsilyl)silane (XI) and chlorine (attempted). A solution of compound XI, 6.4 g. (0.02 mole), in carbon tetrachloride was cooled to -30° and chlorine gas was introduced at a constant rate. After ten minutes of stirring at this temperature there was essentially no change in the concentration of the polysilane XI. A reaction did occur at -15 ± 3° but the monochlorosilane reacted at a rate equal to that of the starting material yielding products resulting from cleavage of more than one trimethylsilyl group. After 1 hr. v.p.c. still showed the presence of starting material, however, tris(trimethylsilyl)chlorosilane was not detected. A more volatile product thought to be bis(trimethylsilyl)dichlorosilane was present.

Reactions

With methylmagnesium iodide. Ten milliliters (0.015 mole) of the Grignard reagent in ether were added to 10.0 g. (0.0354 mole) of the chlorosilane in 75 ml. of THF. After 1 hr. of stirring Color Test I was negative. An additional 0.036 mole of methylmagnesium iodide was added and stirring was continued for 2 hours. Color Test I was positive; the mixture was hydrolyzed with acidified ice and worked up as usual. The dried organic solvents were removed under reduced pressure and the residue was distilled to give 7.2 g. (78%) of tris(trimethylsilyl)methylsilane, b.p. 77-78°/0.3 mm., m.p. 57-59° (mixed m.p.).

Hydrolysis. Twenty grams of tris(trimethylsilyl)chlorosilane were dissolved in 125 ml. of THF and added to an aqueous solution buffered at pH 7 (Beckman 3581 Buffer Solution). This mixture was refluxed overnight, cooled and the organic layer was separated.

Subsequent to drying over anhydrous sodium sulfate, the organic solvents were removed under reduced pressure. Two distillations gave 9.5 g. (67.6%) of pure tris(trimethylsilyl)silanol, b.p. 81-83°/1.5 mm., n_D^{20} 1.4990; d^{20} 0.8668.

Anal. Calcd. for $C_9H_{28}OSi_4$: Si, 42.4; mol. wt., 264.7; MR_D 89.39. Found: Si, 41.8, 42.1; mol. wt., 260.5; MR_D 89.6.

The i.r. spectrum confirmed the structure and showed pertinent bands at the following positions ( ): 2.73(m), 2.91(s), 3.38(s), 3.95(s), 6.94(m), 7.16(m), 7.79(shoulder)(s), 8.04(s), 12.0(s), 13.15(m), 13.45(m), 14.56(m). The ultraviolet spectrum exhibited a band ($_{max}$) at 250 m .

Hydrolysis on basic alumina. The chlorosilane, 12.0 g. (0.042 mole) was dissolved in petroleum ether and added to a column of basic alumina (Matheson, Coleman & Bell, Chromatographic Grade, 80-200 mesh). One liter of petroleum ether eluted, during 6 hours, 2.1 g. of a mixture of the unchanged chlorosilane and the silanol. Continued elution with ethyl acetate gave 6.0 g. (ca. 63%) of tris(trimethylsilyl)silanol, containing ca. 1% impurities. The product was identified by its v.p.c. retention time and i.r. spectrum.

Tris(trimethylsilyl)bromosilane

Preparation from tris(trimethylsilyl)silane and 1-bromobutane

A mixture of 9.6 g. (0.04 mole) of the silicon hydride and excess 1-bromobutane was stirred at room temperature. After 30 min., v.p.c. indicated that no reaction had occurred. The mixture was then heated to ca. 95°, at which time a rapid exothermic reaction was observed.

The excess alkyl bromide was removed directly by simple distillation. The residue, which was shown to be free of starting material, was distilled under reduced pressure to give a sublimable (ca. 85°/0.7 mm.) solid that solidified in the distillation apparatus. The impure compound was transferred to an apparatus suitable for sublimation. Purification by this technique gave 10.3 g. (79%) of tris(trimethylsilyl)bromosilane, m.p. 80-85°.

Anal. Calcd. for $C_9H_{27}BrSi_4$: Br, 24.6. Found: Br, 24.5, 24.4,

From tetrakis(trimethylsilyl)silane (XI) and bromine

A solution of bromine, 0.025 mole, in 30 ml. of dry benzene was added dropwise to 3.21 g. (0.01 mole) of XI in 50 ml. of the same solvent. In the early stages of the reaction the color of the halogen disappeared immediately and an exothermic reaction occurred. Stirring was continued for 30 min. after the addition was completed and an aliquot was removed for v.p.c. analysis. The starting compound (XI) and three products with lower retention times were present.

Tetrahydrofuran (50 ml.) was added and the mixture was treated with excess methylmagnesium iodide. Subsequent to stirring overnight, the reaction mixture was hydrolyzed with acidified ice. The organic layers were separated, dried over anhydrous sodium sulfate and the solvents were removed by distillation at atmospheric pressure. Analysis (v.p.c.) of the residue gave the data summarized in Table 9 below.

Table 9. Products from the Bromination of Tetrakis(trimethylsilyl) silane, Followed by Treatment with Methylmagnesium Bromide.[a]

Product after bromination	Product after Grignard treatment[b]	Relative ratio[c]
$Me_3SiSiBr_3$[d]	$Me_3SiSiMe_3$	20
$(Me_3Si)_2SiBr_2$[d]	$(Me_3Si)_2SiMe_2$	6
$(Me_3Si)_3SiBr$	$(Me_3Si)_3SiMe$	1
$(Me_3Si)_4Si$	$(Me_3Si)_4Si$	14

[a] Data obtained by v.p.c. analysis.

[b] Authentic samples were available.

[c] Ratios of the brominated products were the same as those of methyl derivatives.

[d] Unknown compound, assignment deduced from the previously known methyl derivative.

Reaction with methylmagnesium iodide

The Grignard reagent (0.03 mole) was added to 6.5 g. (0.02 mole) of the bromosilane dissolved in 50 ml. of THF. The mixture was stirred overnight and hydrolyzed with acidified ice. After the usual work-up, the crude product was distilled to give 3.9 g. (75%) of tris(trimethylsilyl)methylsilane, b.p. 76-78°/0.25 mm., m.p. 56-59° (mixed m.p.). The product was also identified by its v.p.c. retention time.

Bis(trimethylsilyl)dichlorosilane

Preparation:

From tris(trimethylsilyl)chlorosilane and phosphorus pentachloride.

A solution of 32 g. (0.13 mole) of tris(trimethylsilyl)silane in excess carbon tetrachloride was stirred overnight to convert the silicon hydride to the chlorosilane. This was followed by addition of 35 g. (0.17 mole) of phosphorus pentachloride. The mixture was refluxed and the slow reaction was followed by v.p.c. After 30 hours of refluxing there was still a significant quantity of unchanged starting material left. Another 15 g. (0.07 mole) of phosphorus pentachloride were added and the reaction was continued for an additional ten hours. The volatile components were removed at atmospheric pressure and the distillation was continued to give 24 g. (ca. 65%) of bis(trimethylsilyl)dichlorosilane, containing about 2% impurities, b.p. 76-77°/10 mm. A portion of this material was redistilled to obtain a pure sample, n_D^{20} 1.4800, d^{20} 0.9708, λ_{max} 233 mμ.

Anal. Calcd. for $C_6H_{18}Cl_2Si_3$: Cl, 28.8; MR_D, 71.46. Found: Cl, 28.4, 28.3; MR_D, 71.85.

Reactions

With methylmagnesium iodide. An excess of the Grignard reagent was added to a solution of 14.5 g. (0.0597 mole) of the dichlorosilane in THF. An immediate exothermic reaction was observed. The mixture was stirred overnight and hydrolyzed with cold dilute acid. Subsequent to the usual work-up, distillation gave 9.4 g. (77%) of octamethyltrisilane, b.p. 174-176° (lit. value (36) b.p. 175°). The product also had the same retention time (v.p.c.) as an authentic sample of the trisilane.

With lithium aluminum hydride. A solution of bis(trimethylsilyl)dichlorodisilane, 12.5 g. (0.05 mole) in 25 ml. of dry ether

was added to 1.3 g. (0.034 mole) of the hydride in 50 ml. of the same solvent. The reaction mixture was refluxed for 5 hours, subsequent to 3 hours of stirring at room temperature. Ten milliliters of petroleum ether were added and the mixture was transferred to a Soxhlet thimble. Extraction with petroleum ether and removal of the solvent gave the crude product which was distilled to give 4.8 g. (60%) of bis(trimethylsilyl)silane, b.p. 65°/45 mm., n_D^{20} 1.4590, d^{20} 0.7620.

Anal. Calcd. for $C_6H_{20}Si_3$: mol. wt., 176.5; MR_D 63.60. Found: mol. wt., 180.2; MR_D 63.31.

The i.r. spectrum showed the usual peaks for Si-Me (see Table 8) and bands at 4.78 and 10.96 τ for the Si-H absorption. The n.m.r. spectrum (neat, with cyclohexane as internal standard) consisted of a singlet at 7.27 τ, due to the hydrogens on silicon and a singlet at 9.82 for the methyl protons. The ratio (C - H: Si - H) was 9:1 (calcd. 9:1). The u.v. spectrum showed no absorption above 210 mμ.

A repeat run gave a 65% yield of bis(trimethylsilyl)silane.

Bis(trimethylsilyl)methylchlorosilane

Preparations

From tris(trimethylsilyl)methylsilane and phosphorus pentachloride. A mixture of 29.5 g. (0.11 mole) of tris(trimethylsilyl)methylsilane and 33 g. (0.16 mole) of phosphorus pentachloride in 125 ml. of carbon tetrachloride was refluxed for 14 hours. After this time, v.p.c. indicated that only a small quantity of the starting polysilane was present. The solvent and phosphorus trichloride were removed

and the distillation was continued to give 3.2 g. of forerun containing a small amount of the expected product and 18.8 g. (85% based on the unrecovered starting material) of bis(trimethylsilyl)methylchlorosilane, b.p. 75-78°/15 mm., n_D^{20} 1.4728 (lit. value (30), b.p. 80.5°/20 mm., n_D^{20} 1.4727). Four grams of unchanged tris(trimethylsilyl)methylsilane were also isolated.

A repeat run gave a 65% yield of the chlorosilane.

From tris(trimethylsilyl)methylsilane and chlorine. A solution of 26.2 g. (0.1 mole) of the polysilane in carbon tetrachloride was cooled to -20° and chlorine gas was bubbled through at a steady rate. The reaction temperature was held at -20 ± 5°, and after 30 min. of stirring v.p.c. indicated that the desired product was also reacting with the halogen yielding a more volatile compound. The temperature was maintained at -25 ± 5° to minimize this undesirable side reaction. When the reaction was complete, the excess chlorine was removed under the reduced pressure of a water aspirator. The solvent and chlorotrimethylsilane were removed and distillation was continued to give 3 g. of forerun, containing ca. one gram of the desired product (detected by v.p.c.), and 15.7 g. (70%) of pure bis(trimethylsilyl) methylchlorosilane.

Hydrolysis of bis(trimethylsilyl)methylchlorosilane

A mixture of 16.5 g. (0.07 mole) of the chlorosilane, 75 ml. of THF and 40 ml. of distilled water was stirred at room temperature for 5 hours. The separated organic layer was washed with water until neutral to litmus, and dried over anhydrous sodium sulfate. The solvents were removed and the residue was distilled to give 8.2 g.

(52.8%) of bis(trimethylsilyl)methylsilanol b.p. 89°/11 mm., n_D^{20} 1.4780.

Anal. Calcd. for $C_7H_{22}OSi_3$: mol. wt. 206.5. Found: mol. wt. 204.1.

The infrared spectrum showed characteristic (40) peaks at the following positions (μ): 2.73(w), 2.95(m), 3.40(m), 3.45(m), 8.03 (s), 11.9(s), 12.8(s), 13.5(s), 14.5(s). The u.v. spectrum showed a high intensity peak at 221 mμ and one of very low intensity at 243 mμ.

Continued distillation gave 2.8 g. of material (b.p. ca. 105°/ 1.0 mm.) which was shown (v.p.c.) to be predominately a single compound (about 97% pure). The infrared spectrum showed, in addition to the usual absorptions for Si-Me, a strong, broad band between 9.6 and 9.8 microns for the Si-O-Si absorption. The product was assumed to be sym-tetrakis(trimethylsilyl)dimethyldisiloxane.

Anal. Calcd. for $C_{14}H_{42}OSi_6$: MR_D, 133.3. Found: MR_D 130.1.

This product had the same v.p.c. retention time as a sample prepared by the decomposition of bis(trimethylsilyl)methylsilanecarboxy acid.[1] The pure compound had the following physical properties: b.p. 103-108°/1.3 mm., n_D^{20} 1.4815 (18).

1,1-Dichlorotetramethyldisilane

From tris(trimethylsilyl)methylsilane and chlorine

A solution of 26.2 g. (0.1 mole) of the polysilane in 150 ml.

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[1] A sample was kindly supplied by C. L. Smith, Iowa State University of Science and Technology, Ames, Iowa.

of carbon tetrachloride was cooled to -20° and chlorine gas was introduced while the temperature was held at -20 ± 5°. The reaction was followed by v.p.c. The excess chlorine was removed when all of the starting material (XII) had reacted and only a small quantity of 2-chloroheptamethyltrisilane was left. The solvent and chlorotrimethylsilane were removed by simple distillation. The residue afforded, upon fractionation, 2.1 g. of forerun which was shown by v.p.c. to contain ca. 1.5 g. of 1,1-dichlorotetramethyldisilane. The distillation was continued to give 11.5 g. of pure 1,1-dichlorotetramethyldisilane, b.p. 56-58°/30 mm., n_D^{20} 1.4518, d^{20} 1.0010.

Anal. Calcd. for $C_4H_{12}Cl_2Si_2$: Cl, 37.8; MR_D 50.43. Found: Cl, 37.69; MR_D 50.47.

The distillation was continued to give 2.1 g. (9.2%) of 2-chloroheptamethyltrisilane.

From tris(trimethylsilyl)methylsilane, sym-tetrakis(trimethylsilyl) dimethyldisilane and phosphorus pentachloride. A mixture of the two polysilanes was prepared as previously described from 0.25 mole of methyltrichlorosilane, lithium and chlorotrimethylsilane. The crude product mixture was chromatographed on neutral alumina. The products were eluted with petroleum ether and this solvent was removed on a rotary evaporator. The residue was dissolved in carbon tetrachloride and transferred to a reaction flask containing 52 g. (0.25 mole) of phosphorus pentachloride. Subsequent to 12 hours of stirring, v.p.c. indicated that all of the two starting compounds had reacted; however, 2-chloroheptamethyltrisilane was the major product. An additional 21 g. (0.1 mole) of phosphorus pentachloride was added

and refluxing was continued for another 17 hours. The solvents and other volatiles were then removed at atmospheric pressure. Distillation gave 18 g. of impure material which was about 90% 1,1-dichlorotetramethyldisilane. Redistillation gave 16 g. (34%) of product (b.p. 51-52/21 mm.) containing a small quantity of a colorless precipitate and possessing an odor indicative of phosphorus compounds. V.p.c. indicated that this product was 1,1-dichlorotetramethyldisilane (ca. 98% pure). The retention time was the same as a previously prepared sample.

The Reactions of Some Silicon Hydrides With Carbon Tetrachloride

A number of silicon hydrides were treated with carbon tetrachloride at room temperature and the reactions were followed by v.p.c. The purpose was only to determine if the hydrides reacted spontaneously thus no attempts were made to determine optimum conditions. The procedure involved the addition of excess carbon tetrachloride to the sample in a vial, and the injection of samples onto the v.p.c. column. In many cases the products were known compounds and were identified by their retention times. The unknown products were assumed to be chlorosilanes. The results of these reactions are given in the table below.

Preparations and Reactions of Some Silylmetallic Compounds

Reactions of tris(trimethylsilyl)silyllithium - prepared from tetrakis (trimethylsilyl)silane (XI) and methyllithium

Table 10. Vapor Phase Chromatography Data for the Reaction of Some Silicon Hydrides With Carbon Tetrachloride.

Compound	Products[a]	Product ratio[b]
$H(Me_2Si)_nH$	$(Cl)H(Me_2Si)_nCl$	
n		
2	H-n-Cl, Cl-n-Cl[c]	2:1
3	H-n-Cl, Cl-n-Cl[c]	6:1
4	H-n-Cl, Cl-n-Cl[c]	24:1
5	H-n-Cl, Cl-n-Cl[c]	30:1
6	H-n-Cl, Cl-n-Cl[c]	3:1
Et_3SiH	No Reaction	
$(Me_3Si)_2SiH_2$	$(Me_3Si)_2SiHCl$[d], $(Me_3Si)_2SiCl_2$[c]	4:1
$(Me_3Si)_2SiMeH$	$(Me_3Si)_2SiMeCl$[c]	
$R_2MeSiSiRMeH$	$R_2MeSiSiRMeCl$[d,e]	

[a] H-n-Cl and Cl-n-Cl represent the compounds $H(Me_2Si)_nCl$ and $Cl(Me_2Si)_nCl$ respectively.

[b] Product ratios are approximated and are for H-n-Cl/Cl-n-Cl.

[c] Authentic samples were available for comparison of retention times.

[d] Unknown compound.

[e] $R = Me_3Si$

The silyllithium compound was prepared in accordance with the procedure of Gilman and Smith (25, 77). The method involves the re-

action of compound (XI) with methyllithium (prepared in ether) in THF: ether (ca. 4:1). The disappearance of the polysilane (XI) was followed by v.p.c., and a 15-20% excess of methyllithium was required to complete the reaction.

With hexachlorodisilane. Tris(trimethylsilyl)silyllithium, prepared from 0.164 mole of tetrakis(trimethylsilyl)silane, was added dropwise to 5.5 g. (0.021 mole) of hexachlorodisilane in 100 ml. of THF at 0°. The solution acquired a brown color that gradually became darker. The addition was completed in 4 hours and stirring was continued for an additional 5 hours. Subsequent to acid hydrolysis, the organic layers were separated and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure and ethanol was added to the residue to cause immediate precipitation. The mixture was cooled at 0° for 1 hr. and filtered to give 23 g. of product, m.p. (in a sealed tube) 265-290°. Sublimation of this material afforded 19.5 g. (77.1%) of tetrakis(trimethylsilyl)silane, 297-305°. A mixed melting point with an authentic sample was not depressed. The v.p.c. retention time of the product was the same as that of the authentic sample. No other crystalline products were isolated from the polymeric residue.

With methyltrichlosilane. The silyllithium compound (0.06 mole) was added to 3.0 g. (0.02 mole) of methyltrichlorosilane in 75 ml. of THF. An exothermic reaction was observed as the addition was carried out over a 3-hour period. After an additional 1 hr of stirring, Color Test I was negative. The mixture was hydrolyzed with dilute acid and worked up as usual. Subsequent to the removal of

the solvents, ethanol was added to the residue which was then cooled at 0° for 30 min. Filtration gave 6.2 g. of impure tetrakis(trimethylsilyl)silane. Purification by sublimation afforded 5.6 g. (58%) of tetrakis(trimethylsilyl)silane, m.p. 295-302° (mixed m.p.).

Removal of the solvents from the mother liquor gave a polymeric residue which was shown (v.p.c.) not to contain any volatile components.

With dichlorodimethylsilane. To a solution of tris(trimethylsilyl)silyllithium (0.09 mole) in a mixture of THF and ether (4:1) was added 6.0 g. (0.046 mole) of dichlorodimethylsilane in 50 ml. of THF. Color Test I was negative immediately after the 30 min. required to complete the addition. Stirring was continued for 1 hr. and the mixture was hydrolyzed with dilute acid. The solvents were removed and ethanol (95%) was added to the residue. Filtration gave 16 g. of impure product, m.p. 265-280°. Upon recrystallization from ethyl acetate-methanol, there was obtained 9.7 g. (69.3%) of tetrakis(trimethylsilyl)silane, identified by a triple melting point and its retention time.

V.p.c. indicated that the mother liquors contained small quantities of 2 other products that were not isolated.

With 1,2-dichlorotetramethyldisilane. The silyllithium was prepared from 0.13 mole of tetrakis(trimethylsilyl)silane and added dropwise to 13.0 g. (0.07 mole) of the dichlorosilane in THF at ca. -70°. The addition was completed in 2 hours and stirring was continued for an additional hour (Color Test I was negative). Acid hydrolysis was followed by the usual work-up. The solvents were

removed and ethanol was added to give 21 g. of solid product, m.p. 250-268°. Fractional sublimation removed 2.5 g. of tetrakis(trimethylsilyl)silane. The residue afforded, after two recrystallizations from ethyl acetate, 17.9 g. (45.3%) of 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane, m.p. 284-288°.

Anal. Calcd. for $C_{22}H_{66}Si_{10}$: Si, 45.9; mol. wt. 611.7. Found: Si, 45.4, 45.5; mol. wt., 604.5.

The i.r. spectrum was consistent with the assigned structure (Table 8). The n.m.r. spectrum (CCl_4-TMS) exhibited single sharp peaks at 9.62 and 9.77. The ratio of internal to terminal Si-Me protons was 1:4.5 (calcd. 1:4.5).

Preparations of tris(trimethylsilyl)silyllithium in the presence of aromatic hydrocarbons

From tetrakis(trimethylsilyl)silane, (XI) lithium and biphenyl. The first preparations of tris(trimethylsilyl)silyllithium by this procedure involved the addition of a small quantity (ca. 0.5 g.) of biphenyl to a mixture of x moles of tetrakis(trimethylsilyl)silane and 4x moles of lithium in tetrahydrofuran (THF). After 5-10 min. of stirring the mixture acquired a green color, indicating the formation of a lithium biphenyl adduct. The disappearance of the polysilane (XI) was followed by v.p.c. and when there was no change in the quantity of this compound another portion (0.3-0.5 g.) of biphenyl was added. The addition of the aromatic hydrocarbon was repeated until all of the tetrakis(trimethylsilyl)silane (XI) was converted to the silyllithium compound. The samples were hydrolyzed

prior to v.p.c. analysis, thus the silyllithium was converted to the known tris(trimethylsilyl)silane. Using this procedure it was determined that approximately a 4:1 molar ratio of the polysilane (XI) to biphenyl was required to complete the reaction. Although the minimum time was not determined, the reactions were completed in 12-15 hours.

In subsequent runs, the total quantity of biphenyl was added at once and the reaction was complete in 8-10 hours. Throughout the reactions the green color of a lithium-hydrocarbon adduct could be seen through the red-brown color of the silyllithium compound. Double titration gave values that were about equal to the sum of the theoritical molarities of biphenyl and the silyllithium. Usually, the solutions were used within 24 hours of preparation.

The yields of tris(trimethylsilyl)silyllithium, determined by conversion to tris(trimethylsilyl)silane (see below) were 85-90%.

From tetrakis(trimethylsilyl)silane (XI), lithium and naphthalene. The procedure was generally the same as that given when biphenyl was used. The ratio of tetrakis(trimethylsilyl)silane (XI) to naphthalene required to complete the reaction was about 3:1. It was difficult to determine the ratio of the starting compound (XI) to the silyllithium compound during the reaction because tris(trimethylsilyl)silane, the hydrolysis product, had almost the same retention time as naphthalene and the dihydronaphthalenes. In addition to the desired product, v.p.c. showed the presence of small quantities of 8-10 biproducts. The yields of the silyllithium were about the same as those from the biphenyl reactions. As in the biphenyl reactions, double titration

gave values that were higher than the theoretical molarity of tris (trimethylsilyl)silyllithium.

From hexakis(trimethylsilyl)disilane and lithium naphthalenide. A solution of 3.0 g. (0.006 mole) of the polysilane in THF was added to 0.02 mole of freshly prepared lithium naphthalenide (1:1 adduct). Stirring was continued for 1.5 hours and the solution was added to 7.6 g. (0.025 mole) of chlorotriphenylsilane in ether at -50°. After 1 hr. of stirring Color Test I was negative. Hydrolysis was then effected by adding dilute acid. Filtration gave 1.1 g. of hexaphenyldisilane, m.p. 363-366° (mixed m.p.).

The combined organic layers were dried over sodium sulfate and the solvents were removed under reduced pressure. The residue was dissolved in petroleum ether and chromatographed on neutral alumina. Elution with the same solvent gave 4.7 g. of impure product. Recrystallization from cold acetone (0°) gave 4.5 g. (75%) of tris (trimethylsilyl)(triphenylsilyl)silane, m.p. 276-279° (mixed m.p.).

Preparations of tris(trimethylsilyl)silylsodium

From tetrakis(trimethylsilyl)silane, sodium and biphenyl or naphthalene. The experimental procedure was essentially the same as those given above for the corresponding lithium compound. The molar ratios were the same, however, longer reaction times (12-15 hours) were required. Derivatizations with chlorotrimethylsilane (see below) indicated that the yields of the silylsodium compound were ca. 85%.

From hexakis(trimethylsilyl)disilane and sodium naphthalenide. A solution of 1.0 g. (0.002 mole) of the polysilane was added to

0.005 mole of sodium naphthalenide during 15 min. Stirring was continued for 45 min. and an aliquot (1 ml.) was hydrolyzed for analysis. The major product (ca. 80%) was shown (v.p.c.) to be tris(trimethylsilyl)silane. A small amount of tetrakis(trimethylsilyl)silane and two products with higher retention times were also present. When a second aliquot was added to trimethylphosphate tris(trimethylsilyl)-methylsilane was the major product.

Derivatization of tris(trimethylsilyl)silyllithium and tris(trimethylsilyl)silylsodium

The silylmetallic compounds used in the following experiments were prepared in the presence of biphenyl or naphthalene as described above. These reactions were run to establish the existence of the silylmetallic compounds. Either aqueous acid, chlorotrimethylsilane, chlorodiphenylmethylsilane or chlorotriphenylsilane were used as derivatizing agents, affording the following known (18) compounds: tris(trimethylsilyl)silane, tetrakis(trimethylsilyl)silane, tris(trimethylsilyl)(triphenylsilyl)silane and tris(trimethylsilyl)(diphenylmethylsilyl)silane, respectively. The silylmetallic compounds, prepared in THF, were added to the chlorosilane in ether. The expected products were identified by their melting points (or boiling point in the case of acid hydrolysis), mixed melting points and by their v.p.c. retention times.[1] Small quantities of hexamethyldisilane (detected by v.p.c.) and 4,4'-bis(trimethylsilyl)biphenyl were formed

[1] Samples were kindly supplied by C. L. Smith, Iowa State University of Science and Technology, Ames, Iowa.

in all reactions. The latter was actually isolated by distillation from two of the hydrolysis reactions. This previously reported (83) product was identified by spectral data and by comparisons of properties with a sample prepared by the reaction of 4,4-dibromodiphenyl with magnesium in the presence of chlorotrimethylsilane. Small quantities of hexaphenyl disilane were isolated from the reactions involving chlorotriphenylsilane. All reactions were run at room temperature unless otherwise stated. Table 11 summarizes the results from several reactions.

Attempted preparation of bis(trimethylsilyl)silyldilithium

To a mixture of 12.84 g. (0.04 mole) of tetrakis(trimethylsilyl) silane (XI) and 2.8 g. (0.4 g.-atom) of lithium in 75 ml. of THF was added 1.54 g. (0.01 mole) of biphenyl. After 5 min. of rapid stirring, an exothermic reaction began and the green color of the lithium-naphthalene adduct was visible. Subsequent to 8 hours of stirring, only a trace of the polysilane (XI) was unchanged. Additional 1.5 g. portions of biphenyl were added after 12 and 24 hours. After 2 days of stirring a small aliquot was hydrolyzed for analysis. V.p.c. showed the presence of tris(trimethylsilyl)silane, as the major product, and less than 1% of a more volatile compound with a retention time nearly equal to that of bis(trimethylsilyl)silane.

The solution was derivatized with chlorotrimethylsilane, hydrolyzed and worked up as usual. Subsequent to the removal of the solvents, 95% ethanol was added to cause precipitation. Filtration gave 10.2 g. of tetrakis(trimethylsilyl)silane, m.p. 300-310°. Concentration of the mother liquor gave 0.5 g. of the same product. Sublimation of

Table 11. Derivatives of Tris(trimethylsilyl)silyllithium and Tris(trimethylsilyl)silylsodium - $(Me_3Si)_3SiM$.

Run	Metal	Hydrocarbon	Reagent	Product	Yield[a]
1	Li	$C_{12}H_{10}$	H_3O^+	$(Me_3Si)_3SiH$	88.9
2[b]	Li	$C_{12}H_{10}$	H_3O^+	$(Me_3Si)_3SiH$	91.0
3	Li	$C_{12}H_{10}$	Me_3SiCl	$(Me_3Si)_4Si$	81.0
4	Li	$C_{12}H_{10}$	Me_3SiCl	$(Me_3Si)_4Si$	82.1
5[c]	Li	$C_{10}H_8$	Me_3SiCl	$(Me_3Si)_4Si$	82.0
6	Li	$C_{12}H_{10}$	$Ph_2MeSiCl$	$(Me_3Si)_3SiSiMePh_2$	42.6
7	Li	$C_{12}H_{10}$	Ph_3SiCl	$(Me_3Si)_3SiSiPh_3$	51.5
8	Li	$C_{12}H_{10}$	Ph_3SiCl	$(Me_3Si)_3SiSiPh_3$	53.2
9	Li	$C_{12}H_{10}$	Ph_3SiCl	$(Me_3Si)_3SiSiPh_3$	62.5
10	Li	$C_{10}H_8$	Ph_3SiCl	$(Me_3Si)_3SiSiPh_3$	52.0

[a] Yields are based on the quantity of tetrakis(trimethylsilyl)silane converted to the silyllithium compound.

[b] Four additional runs gave 85 to 90% yields of silicon hydride.

[c] Run at ca. -35°.

Table 11. (continued)

Run	Metal	Hydrocarbon	Reagent	Product	Yield[a]
11	Na	$C_{10}H_8$	Me_3SiCl	$(Me_3Si)_4Si$	79.5
12	Na	$C_{12}H_{10}$	Me_3SiCl	$(Me_3Si)_4Si$	80.0
13	Na	$C_{12}H_{10}$	$Ph_2MeSiCl$	$(Me_3Si)_3SiSiMePh_2$	46.5
14[c]	Na	$C_{12}H_{10}$	Ph_3SiCl	$(Me_3Si)_3SiSiPh_3$	63.1
15	Na	$C_{12}H_{10}$	Ph_3SiCl	$(Me_3Si)_3SiSiPh_3$	60.0

the combined fractions gave 10.6 g. (81%) of the pure compound, m.p. 318-321° (mixed m.p.). The unpurified residue was shown (v.p.c.) to contain the known 4,4-bis(trimethylsilyl)diphenyl.

Bis(trimethylsilyl)methylsilyllithium

Prepared from tris(trimethylsilyl)methylsilane and methyllithium followed by treatment with dichlorodimethylsilane. The silyllithium compound was prepared from 26.2 g. (0.1 mole) of tris(trimethylsilyl) methylsilane by treatment with methyllithium in accordance with the procedure of Gilman and Smith (79). When the preparation was complete, the silyllithium (in THF:ether, 4:1) was added to 6.5 g. (0.05 mole) of dichlorodimethylsilane in 100 ml. of THF at ca. -70°. The addition was completed in 45 min. (Color Test I was negative) and the mixture was hydrolyzed with dilute hydrochloric acid. The combined organic layers were dried over anhydrous sodium sulfate and the solvents were removed under reduced pressure. Distillation of the residue afforded 9.7 g. of product, b.p. 122°/0.3 mm., which crystallized upon standing in a Dry Ice-acetone bath over night. Recrystallization of the oily solid from ethyl acetone-methanol gave 9.1 g. (41.2%) of 2,4-bis(trimethylsilyl)decamethylpentasilane, m.p. 47-48°. The infrared spectrum showed the expected absorptions for Si-Me (see Table 8).

Anal. Calcd. for $C_{16}H_{48}Si_7$: Si, 44.98; mol. wt., 437.2. Found: Si, 44.7, 45.1; mol. wt., 441.

Prepared from tris(trimethylsilyl)methylsilane and methyllithium followed by treatment with 1,6-dichlorododecamethylhexasilane. Bis(trimethylsilyl)methylsilane (0.03 mole) was added to a solution

of 6.17 g. (0.015 mole) of the dichloropolysilane in 70 ml. of THF (at ca. -70°) during 30 minutes. After 1 hr. of stirring, Color Test I was negative and the mixture was hydrolyzed. The usual work-up followed and the solvents were removed on a rotary evaporator. Upon standing overnight the residue crystallized to an oily solid. Ethanol was added to make a slurry which upon filtration, gave 7.1 g. of impure product, m.p. 65-74°. Two recrystallizations from ethyl acetate-ethanol afforded 4.83 g. (45.2%) of 2,9-bis(trimethylsilyl)cosamethyldecasilane, m.p. 99-100°.

Anal. Calcd for $C_{26}H_{78}Si_{12}$: Si, 46.3; mol. wt., 728. Found: Si, 45.0, 45.2; mol. wt. 730.

The infrared spectrum gave data consistent with the assigned structure (see Table 8). The ultraviolet absorption consisted of a broad band at (λ_{max}) 282.5 mμ.

From tris(trimethylsilyl)methylsilane, lithium and biphenyl followed by treatment with chlorotriphenylsilane (Run 1). The reaction of the metal with the hydrocarbon was initiated in 5 min. by stirring a mixture of 0.5 g. (3.25 moles) of biphenyl, 6.2 g. (0.025 mole) of the polysilane and 0.7 g. (0.1 g.-atom) of lithium in 75 ml. of THF. After 6 hours an aliquot (ca. 5 ml.) was removed and hydrolyzed for analysis. V.p.c. showed the presence of bis(trimethylsilyl)methylsilane as the major product; however, a significant amount of the starting material was unchanged. Subsequent to the addition of another 0.31 g. (2.0 mmoles) of biphenyl, stirring was continued for 4 hours. V.p.c. still showed the presence of a small amount of starting material. Double titration indicated that 0.028

mole of active species were present. The solution was filtered from the excess lithium into an additional funnel, and added to 9.5 g. (0.03 mole) of chlorotriphenylsilane in 50 ml. of dry ether. The brown solution gave a negative Color Test I when the addition was complete. Acid hydrolysis and filtration gave 0.9 g. of hexaphenyldisilane, m.p. 360-363°. A mixed melting point with an authentic samples was not depressed.

The dried organic solvents were removed under reduced pressure. The residue was dissolved in petroleum ether and chromatographed on neutral alumina. Elution with the same solvent gave a heavy oil to which acetone and a crystal of the expected product was added.[1] Upon cooling at 0° there crystallized 5.0 g. of product, m.p. 52-58°. Recrystallization from the same solvent gave 4.8 g. (43.2%) of bis-(trimethylsilyl)(triphenylsilyl)methylsilane, m.p. 64-65° (mixed m. p.). The mother liquors were shown to contain small quantities of tetrakis(trimethylsilyl)silane and 4,4-bis(trimethylsilyl)diphenyl.

Run 2. A mixture of 6.2 g. (0.025 mole) of tris(trimethylsilyl)methylsilane, 0.7 g. (0.1 g.-atom) of lithium, 80 ml. of THF and 1.0 g. (6.5 mmoles) of biphenyl was rapidly stirred for 12 hours. At this time v.p.c. showed that there was no unchanged starting material present. The solution was filtered from the excess lithium and added to chlorotriphenylsilane in ether. A purification procedure similar to that described above gave 7.1 g. (62.5%) of pure

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[1] Ibid.

bis(trimethylsilyl)(triphenylsilyl)methylsilane.

From sym-tetrakis(trimethylsilyl)dimethyldisilane and methyllithium. Three grams (0.008 mole) of the polysilane in 20 ml. of THF was added at once to 0.011 mole of methyllithium in 15 ml. of ether. Aliquots were removed and hydrolyzed for analysis after 30 min. and 2 hours. V.p.c. showed the presence of four components with lower retention times than the starting material. Bis(trimethylsilyl)methylsilane and bis(trimethylsilyl)dimethylsilane were identified as the major products. The reaction was slow and after 24 hours a small amount of starting material was still unchanged.

From sym-tetrakis(trimethylsilyl)dimethyldisilane, lithium, and biphenyl. To a mixture of 1.9 g. (0.005 mole) of the polysilane, 0.7 g. (0.1 g.-atom) of lithium and 50 ml. of THF was added 0.2 g. (1.5 mmoles) of biphenyl. A green color, characteristic of the lithium-biphenyl adduct appeared after ca. 5 min. of rapid stirring. A small portion of the mixture was hydrolyzed for analysis after 2 hours. Bis(trimethylsilyl)methylsilane, tris(trimethylsilyl)methylsilane and tris(trimethylsilyl)dimethyldisilane were shown to be the products of the reaction. Each had the same retention time as authentic samples. After 10 hours of stirring there was no unchanged starting material. An aliquot was then added to chlorotrimethylsilane, and analyzed by v.p.c. Tris(trimethylsilyl)methylsilane and the original starting material, sym-tetrakis(trimethylsilyl)dimethyldisilane were the products.

From sym-tetrakis(trimethylsilyl)dimethyldisilane (attempted). Enough THF was added to a mixture of 3.8 g. (0.01 mole) of the poly-

silane and 0.7 g. (0.1 g.-atom) of lithium to make a thick paste. After 4 hours of stirring there was no noticeable change. The mixture was then heated at 50° for 2 hours with no effect. After stirring overnight the starting compound was recovered quantitatively.

Bis(trimethylsilyl)methylsilylsodium

A mixture of 7.0 g. (0.03 mole) of tris(trimethylsilyl)methylsilane 1.08 g. (7.0 mmoles) of biphenyl, 2.3 g. (0.1 g.-atom) of sodium and 75 ml. of THF was rapidly stirred for 30 min. to initiate the sodium-biphenyl adduct formation. After 15 hours of stirring v.p.c. indicated that the reaction was complete. The solution was filtered from the excess sodium and added to 12.6 g. (0.04 mole) of chlorotriphenylsilane. Subsequent to two hours of stirring, the mixture was hydrolyzed and worked up as usual. The crude products were chromatographed on neutral alumina. Elution with petroleum ether gave a heavy oil, to which acetone and a crystal of the expected product was added. Upon cooling at 0° there crystallized 4.9 g. of impure product. Recrystallization from cold acetone gave 4.8 g. (35.6%) of bis(trimethylsilyl)(triphenylsilyl)methylsilane, m.p. 64-65° (mixed m.p.).

1,1,2-Tris(trimethylsilyl)-1,2-dimethyldisilanyllithium from sym-tetrakis(trimethylsilyl)dimethyldisilane and phenyllithium

To 25.8 g. (0.068 mole) of sym-tetrakis(trimethylsilyl)dimethyldisilane in 100 ml. of THF was added 55 ml. of 1.35 molar (0.07 mole) of phenyllithium. After 18 hours of stirring v.p.c. showed that only a trace of the starting material was unchanged. The silyllithium

compound was then hydrolyzed with cold dilute acid and the combined organic layers were dried over anhydrous sodium sulfate. The residue afforded, subsequent to two distillations, 9.5 g. (46%) of pure 1,1,2-tris(trimethylsilyl)-1,2-dimethyldisilane, b.p. 91°/1.25 mm., n_D^{20} 1.5120, d^{20} 0.8375.

Anal. Calcd. for $C_{11}H_{34}Si_5$: mol. wt., 306.8; MR_D 110.1. Found: mol. wt., 310.5; MR_D 109.5.

In addition to the expected absorptions for Si-Me (Table 8), the infrared spectrum exhibited peaks for the Si-H group 4.86(s) and 11.45(m) (sh) microns. N.m.r. absorptions were found at the following positions (τ): 6.35 (quartet, J = 5.5 cps), 9.33 (intense singlet), 9.50 (doublet J = 5.5 cps) and 9.59 (singlet). These peaks were assigned to the following groups: MeSi-H (hydrogen on silicon), $SiMe_3$, MeSiH (methyl protons) and Me-Si, respectively. The peaks due to the methyl groups were too close to get an accurate ratio of these; however, the Si-H/CH_3 ratio was 1:33 (calcd. 1:33).

Attempted preparation of 2,3-dilithiooctamethyltetrasilane from sym-tetrakis(trimethylsilyl)dimethyldisilane

A mixture of 2.0 g. (5.4 mmoles) of the polysilane in 20 ml. of THF and 5.42 mmoles of phenyllithium (prepared in ether) was stirred at room temperature for 5 hours. An aliquot was removed and hydrolyzed for analysis. V.p.c. showed the presence of 1,1,2-tris(trimethylsilyl)-1,2-dimethyldisilane as the major product. Another 5.4 mmoles of phenyllithium were added and stirring was continued for 30 hours. After this time the mixture was hydrolyzed, worked up as usual and the

organic layer was analyzed by v.p.c.

1,1,2-tris(trimethylsilyl)-1,2-dimethyldisilane, resulting from cleavage of a single trimethylsilyl group, was the only product that was present in any significant quantity.

Pentamethyldisilanyllithium

From octamethyltrisilane and methyllithium, followed by treatment with trimethyl phosphate. To a solution of 58.3 g. (0.29 mole) of octamethyltrisilane in 220 ml. of THF was added 0.3 mole of methyllithium in ether. After 30 min. of stirring the solution acquired a light yellow color. Subsequent to 46 hours of stirring, v.p.c. showed that 10-15% of the starting trisilane was still unchanged. At this point the solution, which gave a positive Color Test I, was transferred to an addition funnel and added dropwise to 0.35 mole of trimethyl phosphate in THF. After 1 hr. of stirring Color Test I was negative and the mixture was hydrolyzed with cold dilute acid. The combined organic layers were dried over sodium sulfate and the solvents were removed at atmospheric pressure. There was isolated (distillation) from the mixture of products 8.8 g. (20%) of hexamethyldisilane. In addition to its boiling point, the product was also identified by its refractive index, i.r. spectrum and v.p.c. retention time.

From octamethyltrisilane, lithium and biphenyl; followed by treatment with chlorodimethylphenylsilane. To a mixture of 10.3 g. (0.051 mole) of octamethyltrisilane, 1.4 g. (0.2 g.-atom) of lithium and 75 ml. of THF was added 1.0 g. (6.5 mmoles) of biphenyl. A green color, characteristic of the lithium-biphenyl adduct, appeared after 2 min. of stirring. An additional 1.3 g. (8.45 mmoles) of biphenyl were added

in two portions to complete the reaction in 24 hours. Double titration indicated that the solution contained 0.048 mole of active species. Subsequent to filtration from the excess lithium, the solution was added to 10.2 g. (0.06 mole) of chlorodimethylphenylsilane in THF at ca. -50°. The addition was carried out during 30 min. and stirring was continued for another 15 min. Color Test I was negative, thus the solution was hydrolyzed and worked up as usual. Most of the volatiles were removed at atmospheric pressure and the distillation was continued under the reduced pressure of a water aspirator to give a mixture containing THF and a product with the same v.p.c. retention time as hexamethyldisilane. Distillation of the residue gave mixtures which were shown by v.p.c. to contain a compound with the same retention time as the known (30) 1-phenyl heptamethyltrisilane.[1]

A partial separation of the impure material gave 1.9 g. of pure 1-phenylheptamethyltrisilane, b.p. 138°/20 mm., n_D^{20} 1.5202 (lit. value (30), b.p. 142°/23 mm., n_D^{20} 1.5204). A quantitative estimation by v.p.c. indicated that the total yield of this product was between 35 and 40%. The unpurified residue also contained four products with higher retention times than 1-phenylheptamethyltrisilane.

From octamethyltrisilane, lithium and biphenyl; followed by treatment with chlorodimethylsilane. The cleavage was carried out as described above with 15.3 g. (0.075 mole) of octamethyltrisilane, 1.4 g. (0.2 g.-atom) of lithium and 2.9 g. (0.019 mole) of biphenyl. The

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[1] The authentic sample was prepared by G. L. Schwebke, Iowa State University of Science and Technology, Ames, Iowa.

reaction was stopped after 15 hours and the solution was added to 14.1 g. (0.15 mole) of chlorodimethylsilane in THF at ca. -70°. When the reaction was complete, the volatiles were removed by simple distillation; the residue was taken up in ether and hydrolyzed with acid. The solvent free residue was distilled to give four impure fractions (3.8 g.) boiling over the range, 85-105°/50 mm. The first fraction (1.5 g.), b.p. 85-90°/50 mm. (168-170°/760 mm.), contained two compounds. The minor component (ca. 10%) was identified by v.p.c. as octamethyltrisilane, the starting material. The peak due to the second component had a lower retention time, and almost overlapped with that of octamethyltrisilane. The infrared spectrum of this fraction showed the usual peaks for Si-Me and a strong absorption for Si-H at 4.74 μ . This compound was probably the expected product, 1-hydroheptamethyltrisilane (lit. value (30) b.p. 61°/22 mm.). The reported boiling point, when extrapolated to atmospheric pressure, is ca. 172°.

The fourth fraction (1.0 g.), b.p. 100-104°/50 mm., contained small amounts of the components in the first fraction and a major product (ca. 80%) with a higher boiling point. The i.r. spectrum of this mixture also exhibited a strong absorption for Si-H (4.73 μ). Since the retention time of the product was a bit lower that of 1,4-dihydrooctamethyltetrasilane, it was thought to be undescribed 1-hydrononamethyltrisilane. This was further supported by the observation that this compound reacts with carbon tetrachloride to give a single product (determined by v.p.c.) while 1,4-dihydrooctamethyltetrasilane gives two products (see Table 10). The undistilled residue (7 g.) contained 3 major products. The i.r. spectrum of the mixture showed

strong absorptions for Si-Me and Si-H (4.74 μ), and a peak of medium intensity (8.95 μ) due to Si-Ph absorption. This latter band was due, at least in part, to 4,4'-bis(trimethylsilyl)diphenyl which was detected by v.p.c. None of these three products had a retention time that corresponded to those of the known compounds, $H(Me_2Si)_nMe$, where n = 4,6 or dodecamethylcyclohexasilane.

Bis(trimethylsilyl)phenylsilyllithium

To a mixture of 20 g. (0.062 mole) of tris(trimethylsilyl)phenylsilane, 2.8 g. (0.4 g.-atom) of lithium and 60 ml. of THF was added, 0.5 g. (3.3 mmoles) of biphenyl. The green color, characteristic of the lithium-biphenyl adduct, appeared after 3 min. of stirring. The reaction was completed in 12 hours by adding 0.5 g. portions of biphenyl after 2 and 8 hours. A hydrolyzed aliquot (0.5 ml.), upon analysis by v.p.c., was shown to contain bis(trimethylsilyl)phenylsilane and a small amount of tris(trimethylsilyl)silane. The ratio of these two was ca. 7:1, respectively. A second aliquot was added to chlorotrimethylsilane and the two major products had the same retention times as tris(trimethylsilyl)phenylsilane, the starting material, and tetrakis(trimethylsilyl)silane. The ratio of these (7:1) two was about the same at that of the two silicon hydrides.

The reaction mixture was added to 24.6 g. 0.08 mole of chlorotriphenylsilane in ether. After 2 hours of stirring Color Test I was negative and the mixture was hydrolyzed with acid. Subsequent to the usual work-up the solvents were removed under reduced pressure, the residue was dissolved in petroleum ether and chromatographed on neutral alumina. The same solvent was used to elute a heavy oil to which ethanol

(95%) was added. Cooling at 0° caused crystallization of 14.6 g. of product, m.p. 240-249°. Two recrystallizations from 95% ethanol gave 12.7 g. (40%) of bis(trimethylsilyl)(triphenylsilyl)phenylsilane, m.p. 257-58.5°.

Anal. Calcd. for $C_{30}H_{38}Si_4$: Si, 22.0; mol. wt., 511. Found: Si, 21.8, 22.3; mol. wt., 508.

The infrared spectrum (CCl_4) was consistent with the assigned structure showing pertinent peaks at the following positions (μ) 3.27(m), 3.39(m), 3.45(m), 6.25(m), 7.0(s), 7.98(s), 8.07(s), 9.10(s). The n.m.r. spectrum showed a multiplet centered at 2.70 τ for the aromatic protons and a singlet at 9.95 due to the methyl protons the ratio of aromatic to methyl protons was 20:18 (calcd. 20:18). The ultraviolet spectrum consisted of a peak at 240 m μ (ε 14,520).

4,4'-Bis(trimethylsilyl)diphenyl (83) was identified (v.p.c.) as a product but was not isolated.

1,4-Dilithiooctaphenyltetrasilane

From octaphenylcyclotetrasilane, lithium and naphthalene, followed by treatment with chlorotrimethylsilane. A reaction was initiated in 2 min. by stirring a mixture of 7.28 g. (0.01 mole) of the cyclotetrasilane, 1.4 g. (0.2 g.-atom) of lithium and 0.26 g. (0.002 mole) of naphthalene. After 40 min., there was no insoluble cyclosilane visible. Stirring was continued for 1.5 hours; the solution was filtered from the excess lithium and derivatized with chlorotrimethylsilane. The mixture was hydrolyzed and worked up as usual. The solvents were removed by rotary evaporation and petroleum ether was added to the residue. Filtration, subsequent to cooling at 0° for 30 min., gave 6.3 g. of impure

product, m.p. 285-291°. Two recrystallizations from benzene-petroleum ether gave 6.0 g. (62%) of pure 1,4-bis(trimethylsilyl)octaphenyltetrasilane, m.p. and mixed m.p. 294-296° (lit. value (84) m.p. 293-296°).

From octaphenylcyclotetrasilane, lithium and biphenyl, followed by acid hydrolysis (Run 1). To a mixture of 7.28 g. (0.01 mole) of octaphenylcyclotetrasilane 1.4 g. (0.2 g.-atom) of lithium and 100 ml. of THF was added 0.3 g. (0.002 mole) of biphenyl. After 20 min. of stirring there was no insoluble cyclosilane. Stirring was continued for an additional 10 min. and the solution was filtered from the excess lithium into a mixture of ice and hydrochloric acid. The combined organic layers were dried over sodium sulfate and the solvents were removed under reduced pressure. Petroleum ether was added to the residue which was then cooled at 0° and filtered to give 5.5 g. of 1,4-dihydrooctaphenyltetrasilane, m.p. 155-160°. Recrystallization from benzene-petroleum ether gave 5.2 g. 53.5% of the pure compound, m.p. 161-162° (mixed m.p.).

Three repeat runs gave 50-60% yields of product.

1,4-Disodiooctaphenyltetrasilane

From octaphenylcyclotetrasilane and sodium naphthalene, followed by acid hydrolysis. A slurry of 8.0 g. (0.011 mole) of 8.0 g. (0.011 mole) of octaphenylcyclotetrasilane in 80 ml. of THF was added to 0.04 mole of sodium naphthalenide during 30 minutes. Stirring was continued for 1.5 hours and the solution was hydrolyzed with saturated ammonium chloride. The combined organic layers were dried over anhydrous sulfate and the solvents were removed under reduced pressure. Petroleum ether was added to the residue and after standing for 20 min. the mixture

was filtered to give 4.0 g. of impure product, m.p. 159-162°. Another 0.5 g. of the crude product was obtained from the mother liquor. The combined fractions were recrystallized from petroleum ether to give 4.4 g. (54.5%) pf pure 1,4-dihydrooctaphenyltetrasilane, m.p. 161-163° (lit. value (45), 160-162°). A mixed melting point was not depressed. Concentration of the original mother liquor followed by sublimation afforded 2.6 g. of naphthalene, m.p. 80-81° (mixed m.p.).

From octaphenylcyclotetrasilane and sodium naphthalenide followed by treatment with chlorotrimethylsilane. The cyclotetrasilane (7.28 g. in 100 ml. of THF) was added to 0.22 mole of sodium naphthalenide in THF. The addition was completed in 1 hr. and stirring was continued for 6 hours. A solution of 0.25 mole of chlorotrimethylsilane in THF was added rapidly. Color Test I was negative after 10 min., and the mixture was hydrolyzed with dilute acid. Subsequent to the usual work-up, the solvents were removed and petroleum ether was added to the residue. Filtration gave 5.65 g. of impure product, m.p. 287-292°. Recrystallization from benzene-petroleum ether gave 5.6 g. (57.5%) of pure 1,4-bis(trimethylsilyl)octaphenyltetrasilane, m.p. 295-297° (lit. value (84) 293-296°) a mixed melting point with an authentic sample was not depressed. Naphthalene was detected by v.p.c. but not isolated.

From octaphenylcyclotetrasilane, sodium and naphthalene or biphenyl followed by treatment with chlorotrimethylsilane. To a mixture of 14.5 g. (0.02 mole) of octaphenylcyclotetrasilane, 4.6 g. (0.2 g.-atom) of sodium in 100 ml. of THF was added 0.5 g. (0.004 mole) of naphthalene. After 10 min. of stirring the solution acquired a

green color characteristic of sodium naphthalenide. The reaction was continued for four hours and the solution was filtered from the excess sodium and derivatized with chlorotrimethylsilane. A purification procedure similar to that described above gave 11.5 g. (59%) of 1,4-bis(trimethylsilyl)octaphenyltetrasilane, m.p. 293-296° (mixed m.p.).

Five repeat runs, using naphthalene or biphenyl, gave 55-60% yields of products upon derivatization with acid or chlorotrimethylsilane.

1,5-Dilithiodecaphenylpentasilane

1:2 Molar ratio of decaphenylcyclopentasilane and lithium naphthalenide. A solution of 0.02 mole lithium naphthalenide (1:1 adduct) in THF was added to a slurry of the cyclosilane (0.01 mole) in THF. The green color of the lithium-naphthalene adduct disappeared immediately upon contact with the polysilane and the red-brown color characteristic of the silyllithium compound was visible. The solution (15 ml.) was added during 10 min., stirring was continued overnight and hydrolysis was effected with cold dilute acid. The usual work-up followed and the dried organic solvents were removed by rotary evaporation. Acetone was added to the residue which was then cooled at 0° for 1 hr., and filtered to give 5.75 g. of impure product. Recrystallization from acetone afforded 5.55 g. (61%) of pure 1,5-dihydrodecaphenylpentasilane, m.p. and mixed m.p. 147-149° (lit. value (84), m.p. 147-149°). The solvent was removed from the original mother liquor and the residue gave, upon sublimation, 1.4 g. (91%) of naphthalene, identified by its melting point and a mixed melting point.

7:1 Molar ratio of decaphenylcyclopentasilane and naphthalene, in the presence of lithium. The reaction was initiated in 5 min. (determined by the appearance of a yellow color) by stirring a mixture of 9.1 g. (0.01 mole) of the cyclosilane, 0.18 g. (1.43 mmoles) of naphthalene, 2.8 g. (0.04 g.-atom) of lithium and 100 ml. of THF. Stirring was continued for 1.5 hr. and the solution was derivatized with chlorotrimethylsilane. Subsequent to hydrolysis and removal of the organic solvents, the residue was taken up in ethyl acetate, cooled and filtered to give 6.8 g. of impure product, m.p. 170-181°. Two recrystallizations from ethyl acetate afforded 6.4 g. (60%) of pure 1,5-bis(trimethylsilyl)decaphenylpentasilane, m.p. 198-200° (lit. value (84), m.p. 197-198°). A mixed m.p. with an authentic sample was not depressed.

In four subsequent runs, yields of 60-65% of this same product were obtained when the reactions were continued from 1-1.5 hours, after the yellow color appeared. When the reactions were continued for longer periods of time a drop in yield was observed and significant quantities of 1,3-bis(trimethylsilyl)hexaphenyltrisilane and 1,2-bis(trimethylsilyl)tetraphenyldisilane (84) were isolated. These were identified by their melting points and by mixed melting points with authentic samples.

1,5-Disodiodecaphenylpentasilane

1:2 Molar ratio of decaphenylcyclopentasilane and sodium naphalenide. A solution of 0.021 mole of sodium naphthalenide in THF (30 ml.) was added (5 min.) to a slurry of 9.1 g. (0.01 mole) of the cyclosilane in THF. Stirring was continued for 6 hours and the solution

was treated with chlorotrimethylsilane. A purification procedure similar to that described above gave 6.7 g. (62.5%) of 1,5-bis(trimethylsilyl)decaphenylsilane, m.p. 197-199° (mixed m.p.).

7:1 Molar ratio of decaphenylcyclopentasilane and naphthalene or biphenyl in the presence of sodium metal. Naphthalene (1.43 mmoles) was added to a mixture of 9.1 g. (0.01 mole) of decaphenylcyclopentasilane and 1.2 g. (0.05 g.-atom) of sodium in 75 ml. of THF. After 3 min. of stirring a yellow color appeared, indicating that the reaction had started. Stirring was continued for a total of 2.5 hours and chlorotrimethylsilane was added until Color Test I was negative. Work-up afforded 6.7 g. (62%) of 1,5-bis(trimethylsilyl)decaphenylpentasilane, m.p. 198-200°.

Six repeat runs, using naphthalene or biphenyl, gave 58-63% yields of the same product. The reactions in which biphenyl was used proceeded faster than the naphthalene catalyzed reactions and were not run longer than 2 hours. If a longer time was used significant quantities (15-20%) of the lower homologs, 1,3-bis(trimethylsilyl)hexaphenyltrisilane and 1,2-bis(trimethylsilyl)tetraphenyldisilane, were isolated subsequent to derivatization with chlorotrimethylsilane.

Preparation of a mixture of silanyllithium compounds from dodecamethylcyclohexasilane

1:2 Molar ratio of dodecamethylcyclohexasilane and lithium naphthalenide. A solution of 0.06 mole of lithium naphthalenide (1:1 adduct) was added at once to 10.5 g. (0.03 mole) of the cyclopolysilane in 75 ml. of THF. Stirring was continued for 24 hours and the solution was hydrolyzed with cold, dilute acid. The dried organic solvents were

removed by rotary evaporation and acetone was added to the residue, which was then cooled at 0° for 1 hour. Filtration gave 8.4 g. (80%) of unchanged dodecamethylcyclohexasilane, identified by its melting point and a mixed melting point.

The infrared spectrum of the solvent free residue showed an absorption band at 4.84 microns, indicating the presence of compounds containing the Si-H group.

From dodecamethylcyclohexasilane, lithium and biphenyl (Run 1). The hydrocarbon (0.5 g.) was added to a mixture of 35.0 g. (0.1 mole) of the cyclosilane 5.0 g. (0.7 g.-atom) of lithium in 150 ml. of THF. After 5 min. of stirring, a green color appeared, indicating that a reaction had started. The disappearance of the cyclosilane was followed by v.p.c. and when there was no change in the concentration of this compound, additional quantities of biphenyl were added. A total of 2.0 g. of the hydrocarbon was added during 24 hours and stirring was continued for 46 hours. The solution, though still containing unchanged starting material, was filtered from the excess lithium into cold dilute acid to cause precipitation of a solid which decomposes above 385°. This material was insoluble in water, alcohol, ethyl acetate, cyclohexane and benzene. The infrared spectrum (KBr) showed strong absorptions for Si-Me indicating that the material was a high molecular weight polymer containing dimethylsilyl units.

The organic layer from the hydrolysis mixture was separated; dried over sodium sulfate and the solvents were removed by rotary evaporation. Distillation to 1.25°/0.1 mm. which were shown (by comparing retention times) to contain the known compounds: $H(Me_2Si)_nH$, where

n = 3,4,5, and 6 and also dodecamethylcyclohexasilane. Distillation at higher temperatures gave mixtures containing four products thought to be the undescribed compounds: $H(Me_2Si)_nH$, where n = 7,8,9 and 10. The infrared spectra of each fraction showed strong absorptions for Si-H and Si-Me only.

Run 2. The reaction was run with 35 g. (0.1 mole) of dodecamethyl, excess lithium and 3.1 g. (0.002 mole) of biphenyl. Stirring was continued for 2 days (cleavage of the cyclosilane was incomplete) and the mixture was treated with chlorotrimethylsilane. Hydrolysis caused precipitation of 4.9 g. of insoluble polymer of the type isolated from Run 1. The dried organic solvents were removed under reduced pressure and the addition of ethanol caused precipitation of a mixture of products. Attempts to obtain pure products by fractional crystallization from ethanol, ethyl acetate, benzene and mixture of these gave impure fractions with melting points up to 200°. The infrared spectrum of several fractions showed absorptions for Si-Me only.

The known[1] compounds, $Me_3Si(Me_2Si)_nSiMe_3$; where n = 3-6,8,9 were identified by v.p.c.

Run 3. The cleavage was carried out with 35 g. (0.1 mole) of dodecamethylcyclohexasilane, excess lithium and 4.5 g. (0.03 mole) of biphenyl. The latter was added in four portions during 72 hours. Stirring was continued for a total of 84 hours and the solution was derivatized with chloropentamethyldisilane. Hydrolysis did not cause

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[1] Authentic samples were generously supplied by Dr. M. Kumada, Kyoto University, Kyoto, Japan.

precipitation of an insoluble polymer as in the first two runs. Work-up afforded the usual mixture of products of the type: $Me_3Si(Me_2Si)_n SiMe_3$, where $n \geqslant 5$. Tedious fractional recrystallizations from ethanol, ethyl acetone, benzene and mixtures of these gave small quantities of pure docosamethyldecasilane and hexacosamethyldodecasilane, identified[1] by their melting points and mixed melting points (lit. value (37), m.p. 113-114° and 153°, respectively. In addition, there was obtained, impure fractions with melting point ranges up to 210°.

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[1] Ibid.

DISCUSSION

Direct Synthesis of Some Linear and Branched Organopolysilanes

In 1964, Gilman and Smith reported (20) the preparation of tetrakis (trimethylsilyl)silane *via* a one-step procedure involving the reaction of tetrachlorosilane with lithium and chlorotrimethylsilane. Smith later used this method for the preparation of tris(trimethylsilyl)methylsilane from methyltrichlorosilane. In view of this stimulating work it was desirable to determine if this attractive method could be extended to the preparation of other polysilanes.

Using a slightly modified procedure (a larger excess of chlorotrimethylsilane was employed), octamethyltrisilane (XXVI) and 2-ethylheptamethyltrisilane (XXVII) were prepared from dimethyldichlorosilane and methylethyldichlorosilane, respectively.

$$MeRSiCl_2 + 4Li + 2Me_3SiCl \xrightarrow{THF} Me_3SiSiMeRSiMe_3$$

XXVI, R = Me
XXVII, R = Et

In four runs the yield of compound XXVI varied between 55 and 70%, and the yield of XXVII from a single experiment was 66%. The homologous tetra- and pentasilanes were detected or identified (by v.p.c.) as minor products from these reactions. In all cases a 50-75% molar excess of chlorotrimethylsilane was used to minimize formation of these and other higher polysilanes.

Optimum conditions were not determined but it is reasonable to expect that the highest yields of trisilane should be obtained when a dilute solution of the dichlorosilane is added to a large excess of chlorotrimethylsilane. It is significant that in the reactions of tetrachlorosilane with lithium and chlorotrimethylsilane a 15-20% molar excess of the latter was sufficient to give high yields (60-65%) of tetrakis(trimethylsilyl)silane (18,78). This difference is probably due in part to steric hinderence to formation of higher branched polysilanes and also to cleavage of these by intermediate silyllithium compounds and by lithium metal. The results of such cleavages would be the formation of species from which tetrakis(trimethylsilyl)silane may be formed. For example it has been shown in this study (see below) that hexakis(trimethylsilyl)disilane reacts with lithium metal to form tris(trimethylsilyl)silyllithium. In contrast, decamethyltertasilane a higher homolog of octamethyltrisilane, is not cleaved by lithium metal. Moreover, steric hinderence to formation of the linear higher polysilanes ($> Si_3$) should be very small as compared to that in the formation of higher branched polysilanes (higher than $(Me_3Si)_4Si$) derived from tetrachlorosilane. On these bases it is reasonable that a large excess of chlorotrimethylsilane is necessary to give satisfactory yields of the monomeric trisilanes.

The predominant reaction path in the formation of octamethyltrisilane (XXVI) and 2-ethylheptamethyltrisilane (XXVII) probably involves initial reaction between the dichlorosilane and the metal with the subsequent formation of a silyllithium compound which couples rapidly with chlorotrimethylsilane.

$$Me_2SiCl_2 + 2Li \longrightarrow Me_2SiClLi + LiCl$$

$$Me_2SiClLi + Me_3SiCl \longrightarrow Me_3SiSiMe_2Cl + LiCl$$

$$Me_3SiSiMe_2Cl + 2Li \longrightarrow Me_3SiSiMe_2Li + LiCl$$

$$Me_3SiSiMe_2Li + Me_3SiCl \longrightarrow Me_3SiSiMe_2SiMe_3 + LiCl$$

A similar mechanism was suggested (18,78) for the formation of tetrakis (trimethylsilyl)silane.

The one-step synthesis described here represents an improved procedure for the preparation of the previously described (36,85) octamethyltrisilane (XXVI). Heretofore, the most satisfactory route (36, 85) to compound XXVI was the three-step synthesis shown in the following sequence of equations.

$$2Me_3SiCl \xrightarrow[\text{or Na}]{\text{Na-K}} Me_6Si_2$$

$$Me_6Si_2 \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} Me_3SiMe_2Cl$$

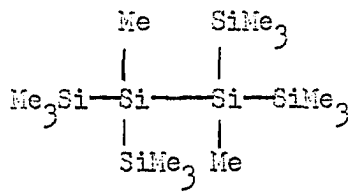
$$Me_3SiSiMe_2Cl + Me_3SiCl \xrightarrow[\text{or Na}]{\text{Na-K}} Me_3SiMe_2SiMe_3$$

A yield of 72% was reported (36) for the third step of the sequence. In comparison, the direct procedure presented here gave 55-70% yields of octamethyltrisilane.

The synthesis of 2-ethylheptamethyltrisilane is reported here for the first time. In addition to the method of preparation, this compound was identified by the normal analytical and spectrometric

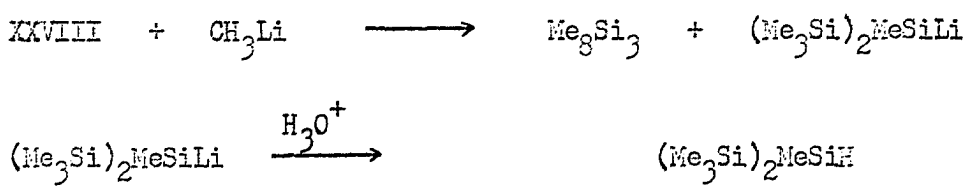
techniques.

Several experiments were run to prepare tris(trimethylsilyl)methylsilane in accordance with the procedure of Gilman and Smith (18,79). The yields (ca. 40%) were comparable to those obtained by Smith. However, during the course of this investigation a second product, namely sym-tetrakis(trimethylsilyl)dimethyldisilane (XXVIII) was isolated from this reaction. The structure assignment was supported by its reaction



XXVIII

with methyllithium followed by acid hydrolysis, to give the known compounds: octamethyltrisilane and bis(trimethylsilyl)methylsilane.



In contrast, phenyllithium effected cleavage of a peripheral Silicon-Silicon bond yielding 1,1,2-tris(trimethylsilyl)-1,2-dimethyldisilanyllithium, which was converted to 1,1,2-tris(trimethylsilyl)-1,2-dimethyldisilane by acid hydrolysis. The latter was readily identified by the usual analytical and spectrometric techniques.

$$\text{XXVIII} + \text{PhLi} \xrightarrow[Et_2O\text{-}THF]{} (Me_3Si)_2MeSiSiMe(SiMe_3)Li$$

$$(Me_3Si)_2MeSiSiMe(SiMe_3)Li \xrightarrow{H_3O^+} (Me_3Si)_2MeSiSiMe(SiMe_3)H$$

An attempt to cleave two trimethylsilyl groups by treating XXVIII with two equivalents of phenyllithium was unsuccessful.

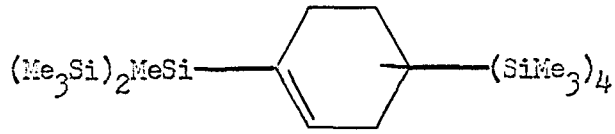
$$\text{XXVIII} + 2\text{PhLi} \xrightarrow{\times} Li(Me_3Si)MeSiSiMe(SiMe_3)Li$$

Encouraged by the successful preparation of the alkylpolysilanes, we next attempted to determine if the method could be extended to the synthesis of phenyl-substituted polysilanes. To achieve this end, phenylmethyldichlorosilane was allowed to react with lithium in the presence of chlorotrimethylsilane. Suprisingly the expected 2-phenyl-heptamethyltrisilane (30) was obtained in only 25% yield.

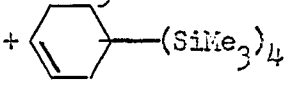
$$MePhSiCl_2 + 4Li + 2Me_3SiCl \xrightarrow[THF]{} Me_3SiMePhSiSiMe_3$$

In addition, there was isolated a solid product which was shown (i.r.) not to contain a phenyl group. This was supported by the n.m.r. spectrum which showed absorptions for olefinic, aliphatic and methyl protons. Expansion (50 cps) of the methyl region showed the presence of five unequivalent trimethylsilyl groups in a ratio of 2:1:1:1:1. The combined data suggested that the product was a compound resulting from reduction of the aromatic nucleus, with the addition of four trimethylsilyl groups to the ring. This type of reaction was not unprecedented since some analagous results (see Historical section) had been reported (57,61,62) from the Dow Corning laboratories. This along with

the n.m.r. data suggested that the compound was bis(trimethylsilyl) tetrakis(trimethylsilyl)cyclohexen methylsilane (XXIX).



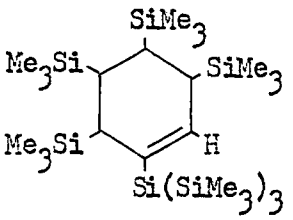
XXIX

Mass spectral data were also consistent with this assignment. The only prominent peaks were exhibited at (m/e): 73 ($Me_3\overset{+}{Si}$), 131, 189 (plus silicon isotopes)($R_2\overset{+}{SiMe}$, R = Me_3Si), 207 (base) (plus Si isotopes), 369 (plus Si isotopes) (+  , and 558(M^+) (low intensity).

Ultraviolet data (λ_{max} 242 m μ) suggested that the double bond was vinylic to the trisilane moiety as shown above. This assignment was based on the observation that substituents such as phenyl and vinyl cause an increase in the λ_{max} (see Historical section). For example, octamethyltrisilane absorbs at 215 m μ (41) while 2-phenyl heptamethyltrisilane absorbs at 241 m μ. This position of the double bond as well as the pattern of substitution on the ring was later confirmed while investigating the structure of an analagous compound (see below).

Smith (18) had previously allowed phenyltrichlorosilane to react with lithium in the presence of chlorotrimethylsilane. Instead of the expected product, a solid compound was isolated which was shown not to contain a phenyl group. The n.m.r. spectrum (Fig. 1) was very similar to that described above for bis(trimethylsilyl)(tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane (XXIX). Since Smith's compound was not identified, it was desirable to determine if it had the same general structure as XXIX. Upon repeating the reaction with

phenyltrichlorosilane, a compound identical to that of Smith's was isolated. A reexamination of the n.m.r. spectrum along with newly acquired u.v. and mass spectral data (Table 12) indicated that the compound was tris(trimethylsilyl)(tetrakis(trimethylsilyl)cyclohex-1-yl)-silane (XXX).



XXX

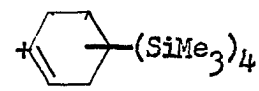
Table 12. Mass Spectral Data for Tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane[a]

m/e	% of Base peak	Assignment
73	88.4	Me_3Si +
74	6.4	___[b]
131	12.0	___
159	5.3	___
173	21.4	___
207	100 (base)	___

[a] Values are given for peaks at least 5% of the base peak.

[b] Silicon isotope for m/e 73.

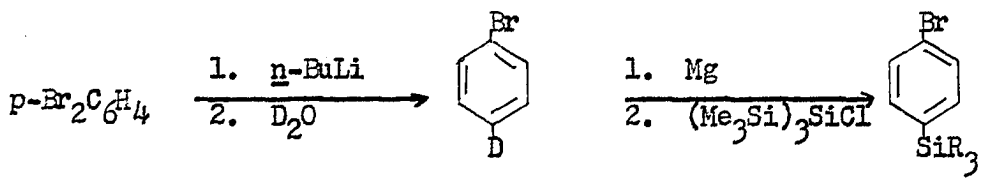
Table 12. (continued)

m/e	% of Base peak	Assignment
208	22.4	c
209	8.5	c
247	22.4	$(Me_3Si)_3Si$ +
281	5.3	——
369	31.0	
370	12.0	d
371	6.4	d
616		M^+

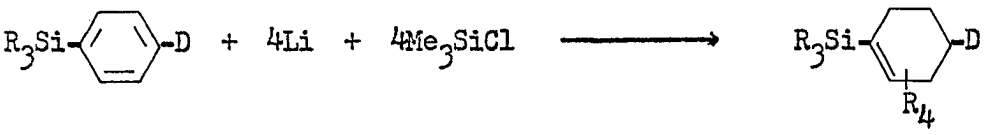
[c] Silicon isotope for m/e 207.

[d] Silicon isotope for m/e 369.

The position of the double bond and the pattern of substitution on the ring were substaniated by n.m.r. studies on tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)-4-d-cyclohexen-1-yl)silane (XXXI) (prepared as shown below).

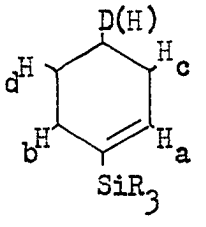


R = $SiMe_3$



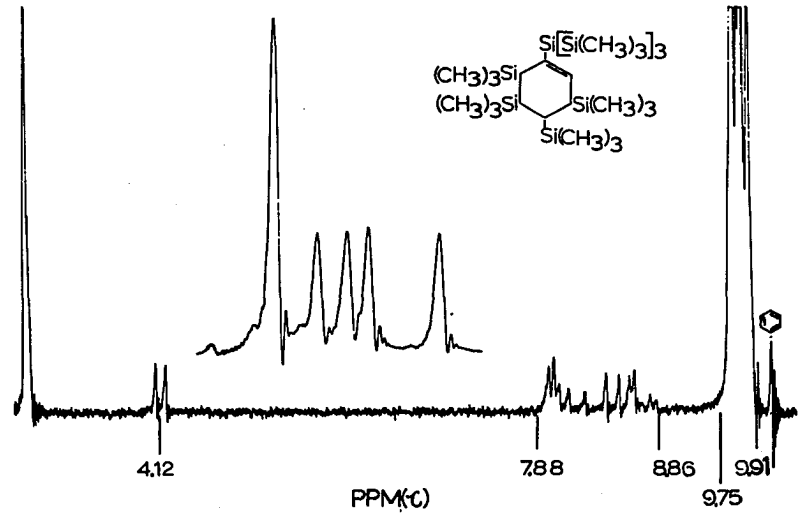
R = $SiMe_3$

It was reasoned that the most probable pattern of substitution should be such that a single trimethylsilyl group was on each of the four aliphatic carbon atoms. If this were the case, then ther would be a single hydrogen on each of the five carbons as shown below. This



proposal could be readily checked by n.m.r. since the spectrum of the deutrated and non-deuterated compounds should be identical, except in the region where the cyclohexyl protons absorb. Theoretically, the spectrum of the deuterated product would be expected to show a total of three doublets due to protons H_b, H_c and H_d. The two compounds did indeed show identical absorptions in the olefinic and methyl regions (see Fig. 1). Figure 2 shows partial spectra (7.7-9.1) for the two compounds. The frequencies of the two allylic protons ($H_b$and H_c) in the deuterated product were very nearly the same (Fig. 2B); a three line pattern was exhibited for these. Double resonance showed the three peaks to be due to two doublets with overlapping lines. Irradiating at the frequency of the olefinic proton (H_a) caused the doublet for $H_c$to collapse to a singlet (Fig. 2C) while irradiating at the frequency of H_a and that of H_d (Fig. 2D) gave singlets for $H_b$and H_c.

Figure 1. Top: Nuclear magnetic resonance spectrum of tris(trimethylsilyl)(3,4,5,6-tetrakis-(trimethylsilyl)cyclohexen-1-yl)silane in carbon disulfide. Bottom: Infrared spectrum of tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane in carbon disulfide.


Si[Si(CH3)3]3
(CH3)3Si
(CH3)3Si
Si(CH3)3
Si(CH3)3
4.12
7.88
8.86
9.91
9.75
PPM(τ)

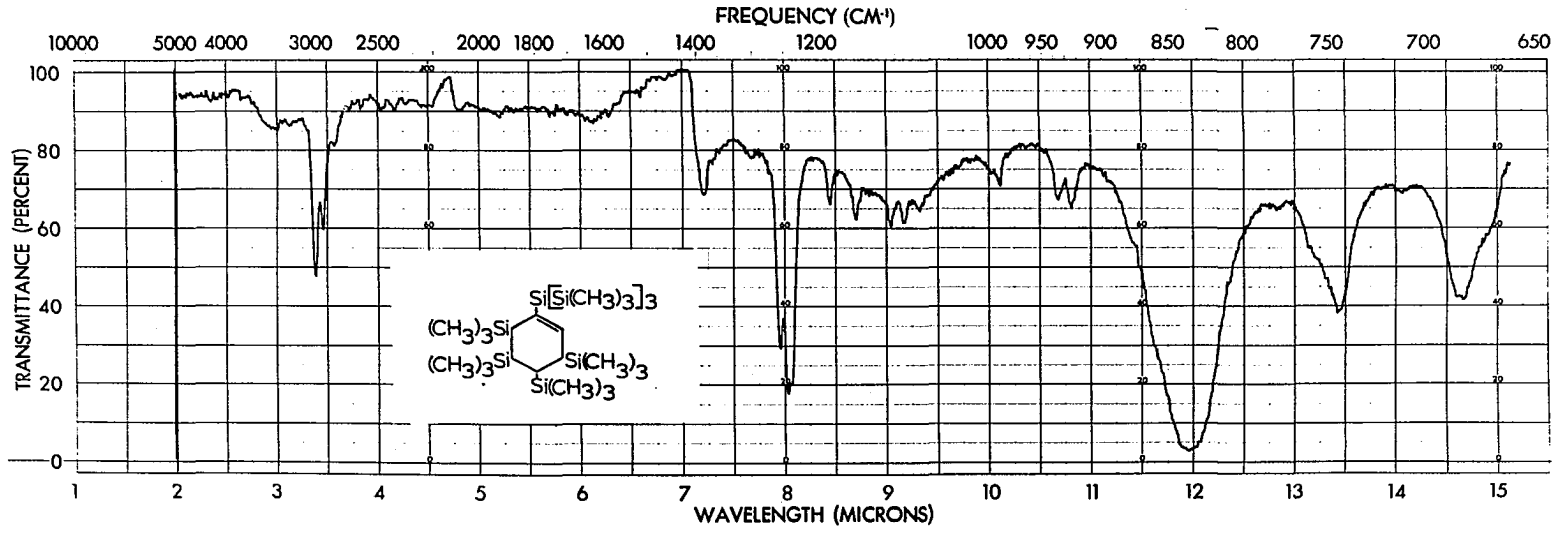

FREQUENCY (CM-1)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
Si[Si(CH3)3]3
(CH3)3Si
(CH3)3Si
Si(CH3)3
Si(CH3)3

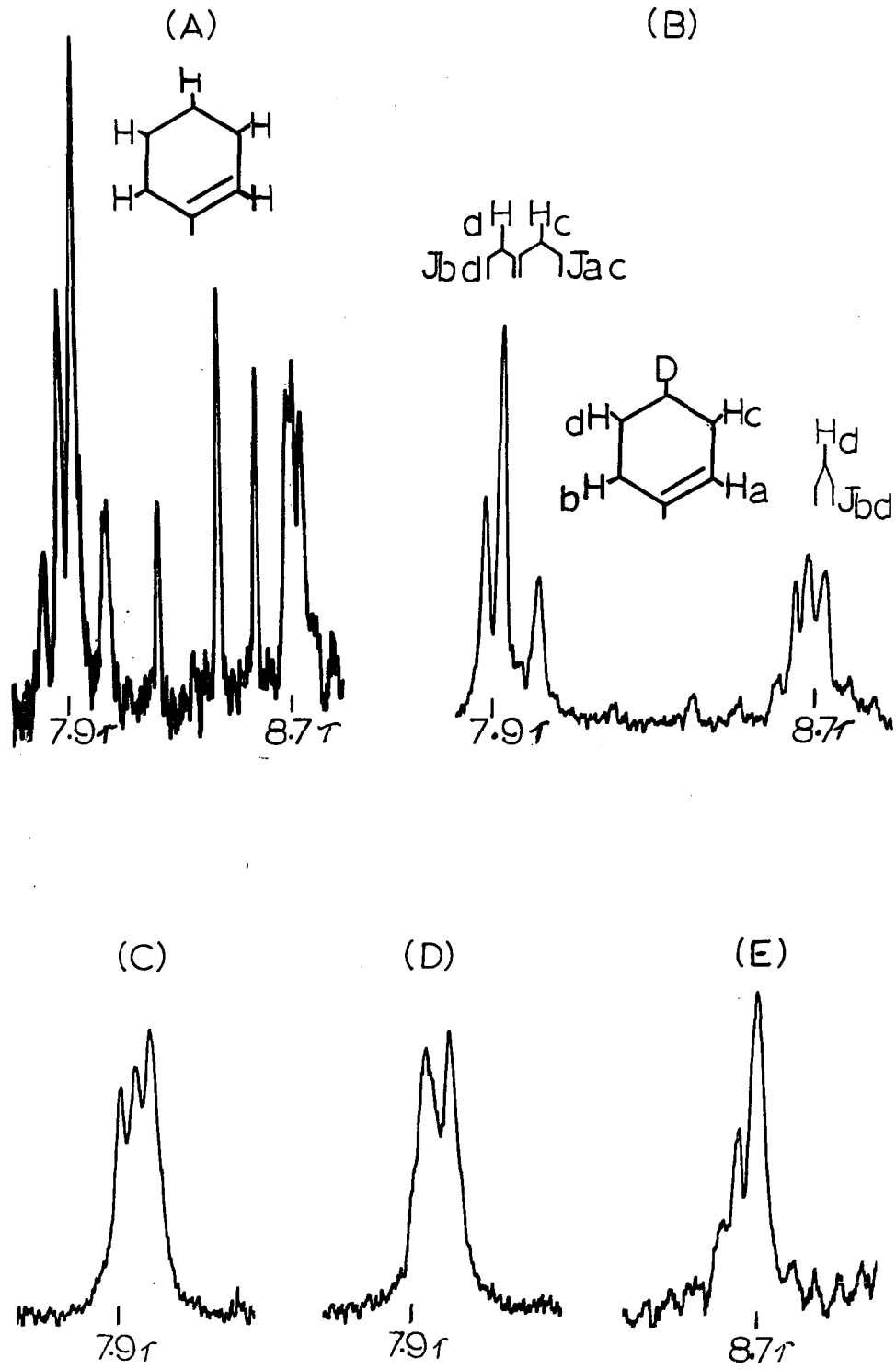
Figure 2A. Nuclear magnetic resonance spectrum for the cyclohexyl protons of tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)silane.

Figure 2B. Nuclear magnetic resonance spectrum for the cyclohexyl protons (Hb,Hc, and Hd) of tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)-4d-cyclohexen-1-yl)silane.

Figure 2C. Spectrum of Hb and Hc while irradiating at the frequency Ha.

Figure 2D. Spectrum of Hb and Hc while irradiating at the frequencies of Ha and Hd.

Figure 2E. Spectrum of Hd while irradiating at the frequencies of Hb and Hc.

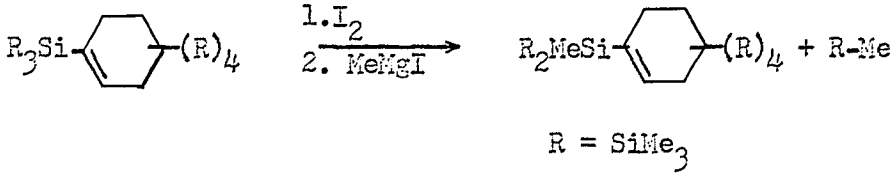

(A)
H
H
H
H
H
7.9τ
8.7τ
(B)
dH Hc
Jbd Jac
D
dH
Hc
bH
Ha
Hd
Jbd
7.9τ
8.7τ
(C)
7.9τ
(D)
7.9τ
(E)
8.7τ

The homoallylic proton (H_d) gave what appeared to be a three line pattern. This was actually shown to be the expected third doublet by first irradiating at the frequency of H_b and H_c causing two of the peaks to collapse to a singlet (Fig. 2 E). Secondly, by scanning up field from TMS, the third peak was shown to be a C^{13}-H side band.

These data therefore established the existence of a single hydrogen atom on each of the four aliphatic ring carbons.

The combined n.m.r. data for the deuterated and non-deuterated compounds also set the position of the double bond to be that assigned on the basis of ultraviolet (λ_{max} 243 mμ) data. The n.m.r. data for a compound with the double bond in any other position would be inconsistent with that obtained.

Bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl) silane (XXIX) was shown, by chemical conversion, to be structually related to tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclo-hexen-1-yl)silane (XXX). Thus the complete structure of XXIX was established.



To determine the general nature of these reduction reactions, the method was extended to a number of other phenylsilanes of the type: Ph_nSiR_{4-n}, where R = Cl, Me_3Si- or Me; and n = 1-4. A detailed study of the reaction of phenyltrichlorosilane was made to test the effect

of a number of variables (see Table 7) on the yield of XXX. The molar ratio of chlorotrimethylsilane and lithium had a pronounced effect on the yield of product. This was due, to some extent, to the conversion of a significant portion of the chlorotrimethylsilane to hexamethyldisilane. The highest yields (85-90%) of XXX were obtained when at least a 50% molar excess of chlorotrimethylsilane and lithium was used. The rate of stirring and reaction temperature had no effect on the final yield, but these did have the expected influence on the rate of the reactions.

Under optimum conditions, phenylmethyldichlorosilane gave 68-70% yields of bis(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)methylsilane. Chlorotriphenylsilane gave a 19% yield of tris(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)(trimethylsilyl) silane (XXXII) and a smaller quantity of material which appeared to contain compounds isomeric to the identified product (see Experimental). The major product from this reaction was a polymeric material containing no phenyl groups.

It was also determined that non-halogenated phenylsilanes react under the same conditions to give the corresponding reduced compounds.

$$Me_3SiPh + 4Li + 4Me_3SiCl \longrightarrow \text{Reduced Products}$$

$$(Me_3Si)_2SiMePh + 4Li + 4Me_3SiCl \longrightarrow \text{XXIX}$$

$$(Me_3Si)_3SiPh + 4Li + 4Me_3SiCl \longrightarrow \text{XXX}$$

$$Ph_3SiSiMe_3 + 12Li + 12Me_3SiCl \longrightarrow \text{XXXII} + \text{Polymer}$$

$$Ph_4Si + 16Li + 16Me_3SiCl \longrightarrow \text{Polymer}$$

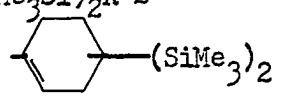
The reaction with phenyltrimethylsilane gave three major products (detected by v.p.c.) that co-distilled during attempted separation. It was not determined whether the compounds were isomeric cyclohexenes or if one or more of these were cyclohexadienes.

The reaction of tetraphenylsilane under these conditions gave polymeric materials only. It thus appears that it is sterically impossible to place more than three of these bulky tetrasilylcyclohexene groups around a single silicon atom.

In connection with these studies, a compound containing two tetrasilylcyclohexene groups was prepared by Shiina.[1] Two isomeric products were isolated.

$$Ph_2SiR_2 + Li + Me_3SiCl \longrightarrow (Me_3Si)_2R'2$$

R = Cl or Me_3Si-

R' =  $(SiMe_3)_2$

The rates of the reactions involving the non-halogenated compounds were slower than those of the corresponding chlorosilanes. This suggested that the electronegative chlorine atoms caused electrons to be drawn (by resonance) from the phenyl group towards silicon as shown below. This may explain the ease with which these phenylsilanes are reduced as compared to benzene and alkylbenzenes (see the Historical section).

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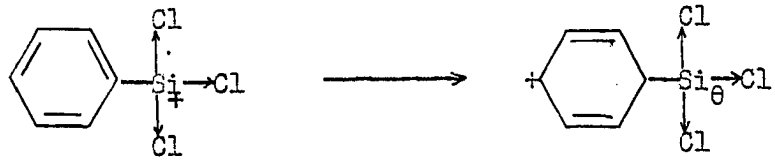
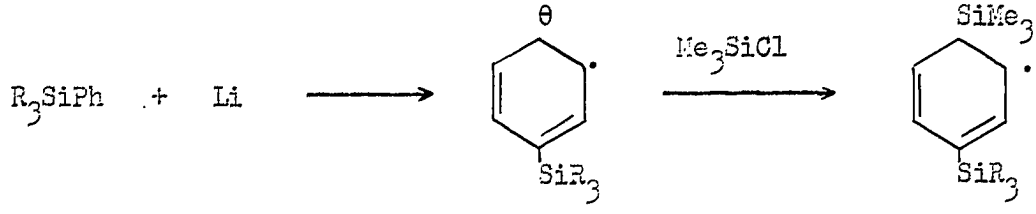
[1] K. Shiina, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of some phenylsilanes with lithium and chlorotrimethylsilane. Private communication. 1966.

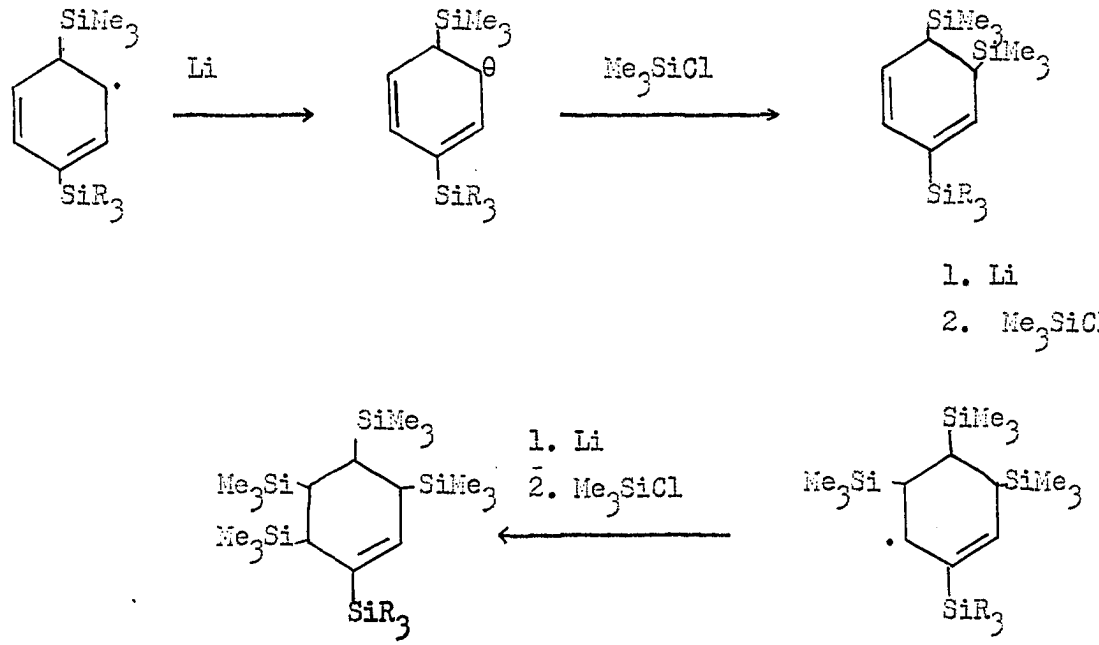


Since all of the phenylsilanes employed were reduced, it appears that this type of reaction is general for phenyl-substituted monosilanes and phenyl-substituted polysilanes in which the Si-Si bonds are not readily cleaved by lithium.

The most reasonable mechanism for the formation of these novel compounds is one similar to that postulated by Weyenberg and co-workers[1] for the formation of tetrasilylcyclohexenes from substituted benzenes. The proposed path involves the formation of an anion radical followed by initial 3,4-disilylation with the formation of a conjugated diene which undergoes further disilylation. Although the scheme shows lithium to be the only reducing agent, an anion radical may possibly be active in this respect. Also, the formation of intermediate dianions cannot be ruled out.



[1] D. R. Weyenberg, The Dow Corning Corporation, Midland, Michigan. Information on the mechanism for the formation of tetrasilylcyclohexenes. Private communication. 1966.



Since it is well known (86) that ether is a relatively poor solvent for anion radical formation, it was desirable to investigate its use for the direct preparation of phenyl-substituted polysilanes. It was hoped that reduction of the phenyl group would be retarded. The first attempt was the preparation of tris(trimethylsilyl)phenylsilane. Ether alone proved to be unsatisfactory and the addition of a small amount of THF (ca. 10-15%) was necessary to initiate the reaction which then proceeded smoothly giving the desired product in 52% yield.

In subsequent runs, the reactions were initiated best by first using a lower ratio of ether:THF (ca. 2:1). When the reaction started, enough ether was added to make the ratio of ether:THF about 9:1. Using this general method, tris(trimethylsilyl)phenylsilane, 2-phenylheptamethyltrisilane and bis(trimethylsilyl)diphenylsilane were prepared in satisfactory yields from phenyltrichlorosilane, phenylmethyldi-

chlorosilane and diphenyldichlorosilane,[1] respectively.

$$PhSiCl_3 + 6Li + 3Me_3SiCl \xrightarrow[Et_2O\text{-}THF]{} (Me_3Si)_3SiPh \quad 50\text{-}52\%$$

$$PhMeSiCl_2 + 4Li + 2Me_3SiCl \longrightarrow (Me_3Si)_2SiMePh \quad 48\text{-}50\%$$

$$Ph_2SiCl_2 + 4Li + 2Me_3SiCl \longrightarrow (Me_3Si)_2SiPh_2 \quad 65\%$$

The reduced product from phenyltrichlorosilane was isolated in only 2-3% yield. 2-Phenylheptamethyltrisilane was previously prepared in 32% yield by the coupling reaction shown below (30).

$$PhMeSiCl_2 + 2Me_3SiCl + 4Na \longrightarrow (Me_3Si)_2SiPhMe \quad 32\%$$

Tris(trimethylsilyl)phenylsilane (19) and bis(trimethylsilyl)diphenylsilane (84) were previously prepared, along with a number of other products, by the lithium cleavage of decaphenylcyclopentasilane.

During this study, tris(trimethylsilyl)phenylsilane was also prepared (25%) by the reaction of phenyltrichlorosilane with magnesium and chlorotrimethylsilane. A second highly-branched compound, sym-tetrakis(trimethylsilyl)diphenyldisilane, was isolated (3%) from this same reaction. This compound was identified by the usual spectrometric and analytical techniques.

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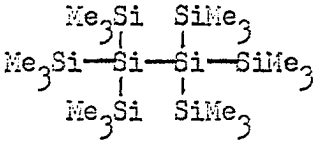
[1] K. Shiina, Iowa State University of Science and Technology, Ames, Iowa. Information on the preparation of bis(trimethylsilyl) diphenylsilane. Private communication. 1966.

$$PhSiCl_3 + 3Mg + 3Me_3SiCl \xrightarrow{THF} (Me_3Si)_3SiPh + (Me_3Si)_2SiPhSiPh(SiMe_3)_2$$

Preparations and Reactions of Hexakis-(trimethylsilyl)disilane

With the successful preparation of the highly-branched and symmetrical hexakis(dimethylsilyl)disilane, from tetrachlorosilane, lithium and chlorodimethylsilane (p. 7) our attention was turned to synthesizing the trimethylsilyl analog; hexakis(trimethylsilyl)disilane (XXXIII).



XXXIII

The direct approach using tetrachlorosilane or hexachlorodisilane gave tetrakis(trimethylsilyl)silane as the only isolable product.

Starting with tris(trimethylsilyl)silyllithium (XIX), compound XXXIII was synthesized by a number of procedures that gave high yields of hexaphenyldisilane from triphenylsilyllithium (2). Initially, the experiments were run at room temperature and hexakis(trimethylsilyl) disilane was isolated in very low yields (5-10%); tetrakis(trimethylsilyl)silane (XI) was the major product (50-75%). The methods are shown in the following equations.

$$2(Me_3Si)_3SiLi + \tfrac{1}{2}I_2 \xrightarrow{25^\circ} XI + (Me_3Si)_6Si_2$$

XXXIII (9-10%)

$$2XIX + BrCH_2CH_2Br \xrightarrow{25^\circ} XI + XXXIII$$

(6-7%)

$$XIX + (Me_3Si)_3SiCl \xrightarrow{25^\circ} XI + XXXIII$$

(7%)

$$2XIX + HgCl_2 \longrightarrow XI + XXXIII$$

(5%)

After running these reactions at room temperature, the formation of XI was readily explained when it was determined that XIX reacts rapidly with XXXIII to form XI (vide infra). Subsequently, the first three reactions (as given above) were run at ca. -70°; an increase in the yield of XXXIII and a corresponding decrease in the yield of XI were realized. In three runs, using 1,2-dibromoethane, the desired product (XXXIII) was isolated in 40-50% yields. From single experiments, the reactions with iodine and tris(trimethylsilyl)chlorosilane gave 20 and 25% yields of XXXIII.

The preparation of XXXIII by the reaction of tris(trimethylsilyl)-chlorosilane with magnesium also gave a mixture in which tetrakis(trimethylsilyl)silane was the major product. Thus, the reaction of tris(trimethylsilyl)silyllithium with 1,2-dibromoethane (at ca. -70°) proved to be the method of choice.

Although hexakis(trimethylsilyl)disilane was initially obtained in low yields, we were able to study the chemical properties of XXXIII by running

small scale reactions and determining their course by v.p.c. analysis. All of these reactions involved Si-Si bond cleavage; due to the high degree of symmetry in the molecule, only three paths were available. These are shown below.

$$(Me_3Si)_3SiSi(SiMe_3)_3 \quad (\text{XXXIII}) + X\text{-}Y \xrightarrow{(a)} (Me_3Si)_3SiX + (Me_3Si)_3SiY$$

$$\text{XXXIII} + X^{+}\!-\!Y^{-} \xrightarrow{(b)} RY + R_3SiSiR_2X$$

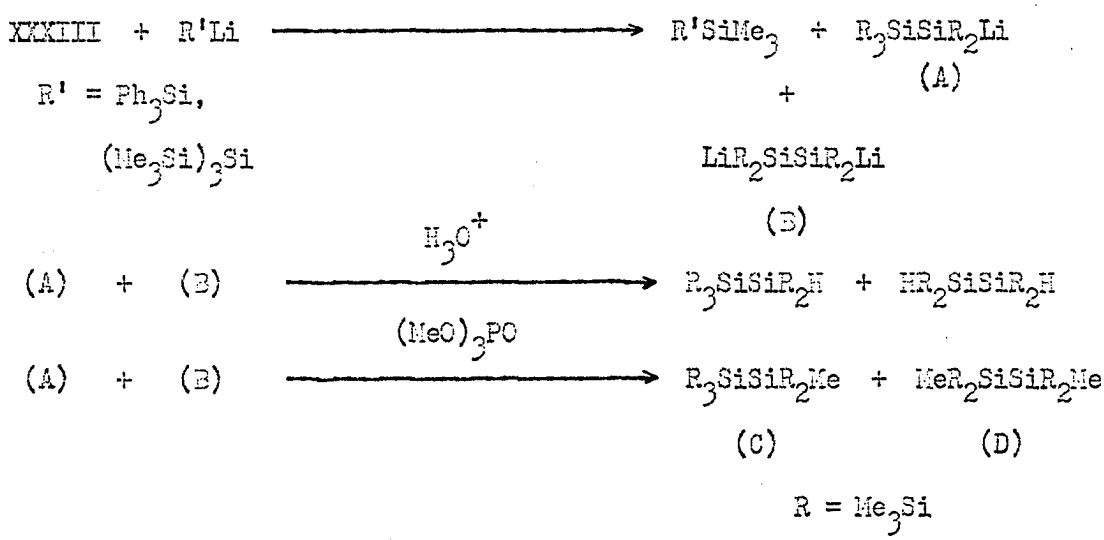
$$\text{XXXIII} + X^{+}\!-\!Y^{-} \xrightarrow{(c)} RX + R_3SiSiR_2Y$$

$$R = Me_3Si$$

It is highly improbable that a reaction would proceed by path (c) since the expulsion of the highly unstable trimethylsilylanion would be involved.

Methyllithium reacted with XXXIII by path (a) affording the known tris(trimethylsilyl)silyllithium and tris(trimethylsilyl)methylsilane. The former was converted by acid hydrolysis, to tris(trimethylsilyl)-silane. Probably for steric reasons, the bulkier triphenylsilyllithium and tris(trimethylsilyl)silyllithium (XIX) reacted with XXXIII by path (b). This was determined by identifying the known compounds, 1,1,1-trimethylsilyl-2,2,2-triphenyldisilane and tetrakis(trimethylsilyl)silane. For the reaction involving tris(trimethylsilyl)silyllithium, chemical evidence was obtained which indicated that the new silyllithium compounds were those shown below. Products (A) and (B), upon acid hydrolysis, gave two compounds that were shown (i.r.) to possess the Si-H group. Treatment of (A) and (B) with trimethyl phosphate gave products

(C) and (D). The latter is a known compound and was identified by v.p.c. Product (C) had a higher retention time than (D) and thus was assumed to be the compound resulting from cleavage of a single trimethylsilyl group from XXXIII.



In the reaction of XXXIII with triphenylsilyllithium, a large excess of the latter was used. The resulting product was believed to be the dilithium compound formed by cleavage of adjacent trimethylsilyl groups.

The reaction of tris(trimethylsilyl)silyllithium with XXXIII by path (a), although highly improbable for steric reasons, cannot be excluded since it would only regenerate starting materials.

Chlorine and bromine reacted with hexakis(trimethylsilyl)disilane (XXXIII) by path (b), which is equivalent to path (c), effecting cleavage of a peripheral Si-Si bond. The resulting bromosilanes were treated with methylmagnesium iodide giving the known sym-tetrakis(trimethylsilyl)dimethyldisilane (designated above as product D) and the product resulting from cleavage of only one trimethylsilyl group.

Compound XXXIII was also treated with methylmagnesium iodide and phenylmagnesium bromide (in THF-ether) in hopes of preparing the first stable silyl Grignard reagent; however, no reaction occurred during a long contact time.

Compound XXXIII was also found to be stable to basic alumina under conditions that some other organopolysilanes undergo cleavage (84,86).

Somewhat surprisingly, hexakis(trimethylsilyl)disilane (XXXIII) reacted rapidly with lithium metal in THF to give tris(trimethylsilyl)-silyllithium. No reaction occurred in ether. As mentioned in the Historical section, many unsuccessful attempts to cleave Si-Si bonds of alkylpolysilanes with this metal have been reported and the presence of one or more phenyl groups was believed to be necessary for cleavage to occur. The facile cleavage of XXXIII is undoubted associated with the formation of a stable silyllithium compound from both fragments.

Preparations and Reactions of Some Linear and Branched Halopolysilanes

Tris(trimethylsilyl)chlorosilane (XXXIV) was initially prepared in 49 and 50% yields by the reaction of tris(trimethylsilyl)silane (XVII) with phosphorus pentachloride. In addition to the usual analytical procedures, the product was identified by its conversion to the known (79) tris(trimethylsilyl)methylsilane.

$$\underset{\text{XVII}}{(Me_3Si)_3SiH} + PCl_5 \longrightarrow \underset{\text{XXXIV}}{(Me_3Si)_3SiCl}$$

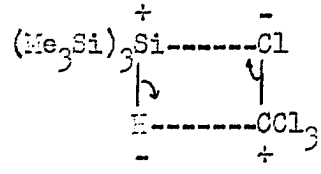
$$\text{XXXIV} + MeMgI \longrightarrow (Me_3Si)_3SiMe$$

Since it had been determined that tris(dimethylphenylsilyl)silane reacted spontaneously with carbon tetrachloride to give what was suspected to be a chlorosilane, an investigation of this method for the preparation of tris(trimethylsilyl)chlorosilane (XXXIV) was undertaken. This proved to be an excellent synthetic procedure affording XXXIV in 85-90% yields.

$$(Me_3Si)_3SiH + CCl_4 \longrightarrow (Me_3Si)_3SiCl + HCCl_3$$

The reactions proceeded rapidly and were completed by simply removing excess carbon tetrachloride by distillation. Chloroform was identified by v.p.c. as the second product of the reactions.

The reaction mechanism probably involves a four-centered transition state similar to that postulated by West and co-workers (34) for the formation of halosilanes from silicon hydrides and triphenylmethyl halides.



Attempts were made to prepare tris(trimethylsilyl)chlorosilane (XXXIV) by a more direct procedure involving the reaction of tetrakis(trimethylsilyl)silane (XI) with phosphorus pentachloride. Only trace amounts of the desired monochlorosilane were detected by v.p.c. The major products were compounds resulting from cleavage of two and three trimethylsilyl groups from the starting material (XI).

$$(Me_3Si)_4Si + (XS)PCl_5 \xrightarrow[\text{or } C_2H_4Cl_4]{CCl_4} (Me_3Si)_nSiCl_{4-n}$$

The known bis(trimethylsilyl)dichlorosilane (n = 2) was identified by v.p.c. as one of the major products of the reaction. The second and more volatile product was believed to be the undescribed 1,1,1-trichloro-2,2,2-trimethyldisilane. Tris(trimethylsilyl)chlorosilane reacted with phosphorus pentachloride at a rate comparable to that of the starting material (XI), and thus was not present in any significant quantity during any stage of the reactions. The data indicated that this reaction would be practical for the preparation of the trichloro compound.

Similarily, bromine reacted with tetrakis(trimethylsilyl)silane to give compounds resulting from cleavage of two and three trimethylsilyl groups as the major products. Again the monohalogenated compound was the minor component. The ratio of products is given in the experimental section. The bromo compounds were identified by their conversion to the known methyl derivatives.

$$(Me_3Si)_4Si + (XS)Br_2 \longrightarrow (Me_3Si)_nSiBr_{4-n}$$

$$(Me_3Si)_nSiBr_{4-n} \xrightarrow{MeMgX} (Me_3Si)_nSiMe_{4-n}$$

$$n = 1 - 3$$

The monobromosilane, tris(trimethylsilyl)bromosilane was however, conveniently prepared by the reaction of tris(trimethylsilyl)silane (XVII) with 1-bromobutane. Methylation of the previously undescribed bromosilane afforded the known tris(trimethylsilyl)methylsilane (79).

$$\underset{\text{XVII}}{(Me_3Si)_3SiH} + \underline{n}\text{-}C_4H_9Br \longrightarrow \underset{79\%}{(Me_3Si)_3SiBr} + C_4H_{10}$$

$$(Me_3Si)_3SiBr + MeMgI \longrightarrow (Me_3Si)_3SiMe$$

In contrast to the reaction of XVII with carbon tetrachloride, that with the alkyl bromide did not proceed spontaneously at room temperature and required heating to ca. 95°.

Bis(trimethylsilyl)dichlorosilane (XXXV) was prepared by the sequence shown below. This compound was identified by elemental analysis and by its conversion to the known (36) octamethyltrisilane. Reduction with lithium aluminum hydride (LAH) gave bis(trimethylsilyl)silane, which is reported here for the first time.

$$(Me_3Si)_3SiH \xrightarrow{CCl_4} (Me_3Si)_3SiCl \xrightarrow{PCl_5} (Me_3Si)_2SiCl_2$$

XXXV

$$XXXV + LAH \longrightarrow (Me_3Si)_2SiH_2 \quad (60\%)$$

$$XXXV + 2MeMgI \longrightarrow (Me_3Si)_2SiMe_2$$

In view of the facile reactivity of tris(trimethylsilyl)silane with carbon tetrachloride we decided to investigate the general scope of the reaction. A number of available alkyl-substituted silicon hydrides were treated with carbon tetrachloride and their reactivity was determined by v.p.c. analysis. The results of this study are given in the Experimental section (Table 10, p.87). Triethylsilane was the only compound that was totally unreactive, even under refluxing conditions. These reactions were much slower than that of tris(trimethylsilyl)silane and the reactivities dropped as the branching decreased. That is, the tertiary (Si_3SiH) silicon hydrides ($SiSiH > R_3SiH$, $R \neq Si$)

were the least reactive.

Like triethylsilane, triphenylsilane was unreactive. The available phenylated polysilanes containing the Si-H group were not volatile enough to be analyzed by v.p.c.

In contrast to the chlorination of tetrakis(trimethylsilyl)silane, the reaction of tris(trimethylsilyl)methylsilane with phosphorus pentachloride gave good yields (65-85%) of the known (36) monochlorinated product, bis(trimethylsilyl)methylchlorosilane. Secondary Si-Si bond

$$(Me_3Si)_3SiMe + Cl_2 \xrightarrow{(PCl_5)} (Me_3Si)_2SiMeCl + (Me_3Si)SiMeCl_2$$

cleavage to give the dichloro compound was controlled better when the reaction was carried out with chlorine below -20°.

The dichloropolysilane was readily prepared by using excess quantities of the chlorinatine reagents. This compound was not obtained free of contaminating phosphorus compounds when the pentachloride was used. For this reason chlorine was the reagent of choice.

sym-Tetrakis(trimethylsilyl)dimethyldisilane also reacted with phosphorus pentachloride to give bis(trimethylsilyl)methylchlorosilane.

$$(Me_3Si)_2MeSiSiMe(SiMe_3)_2 \xrightarrow{PCl_5} 2(Me_3Si)_2MeSiCl$$

Some Reactions of Tris(trimethylsilyl)-silyllithium and Bis(trimethylsilyl)-methylsilyllithium

Attempts were made to prepare some highly branched organopolysilanes by the reaction of tris(trimethylsilyl)silyllithium with dimethyldichloro-

silane, methyltrichlorosilane and hexachlorodisilane. Surprisingly, these reactions gave high yields of tetrakis(trimethylsilyl)silane as the only isolable product.

$$2(Me_3Si)_3SiLi + Cl_2SiMe_2 \longrightarrow (Me_3Si)_4Si$$

XIX XI (69%)

$$XIX + RSiCl_3 \longrightarrow XI$$

R = Me (58%)
R = Cl_3Si (77%)

The formation of such high yields of XI was readily understandable when it was later determined that hexakis(trimethylsilyl)disilane undergoes a rapid reaction with tris(trimethylsilyl)silyllithium (XIX) with the formation of compound XI. This suggested that a compound resulting from the introduction of only a single tris(trimethylsilyl)silyl group would react rapidly with the silyllithium compound (XIX) under the conditions (room temperature or 0°) of the reaction. Also, the introduction of a second or third of these bulky groups around the central silicon was probably extremely slow, if not impossible.

More success was realized when the chlorine atoms were on adjacent dimethylsilyl groups. Thus, the expected 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane was obtained from 1,2-dichlorotetramethyldisilane as shown below.

$$2(Me_3Si)_3SiLi + Cl(Me_2Si)_2Cl \longrightarrow (Me_3Si)_3Si(Me_2Si)_2SiR_3$$

R = $SiMe_3$

As would be expected, steric problems were not as great with bis(trimethylsilyl)methylsilyllithium (XII) and this compound reacted with dichlorodimethylsilane to give 2,4-bis(trimethylsilyl)decamethylpentasilane in 41% yield. Similarily, the silyllithium compound was treated with 1,6-dichlorododecamethylhexasilane in 45% yield.

$$(Me_3Si)_2MeSiLi + Cl_2SiMe_2 \xrightarrow{-70^\circ} (Me_3Si)_2MeSiSiMe_2SiMe(SiMe_3)_2$$

XII

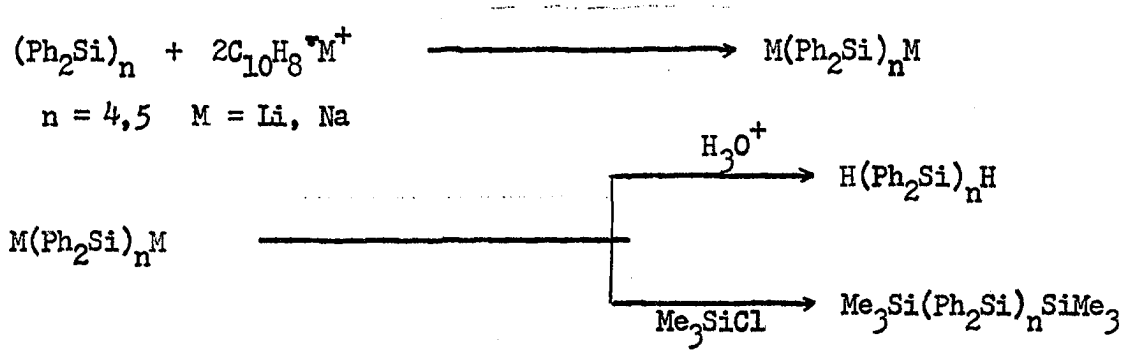
$$XII + Cl(Me_2Si)_6Cl \xrightarrow{-70^\circ} (me_3Si)_2MeSi(Me_2Si)_6SiMe(SiMe_3)_2$$

Preparation of Some Silylmetallic Compounds in the Presence of Alkali Metal-Aromatic Hydrocarbon Adducts

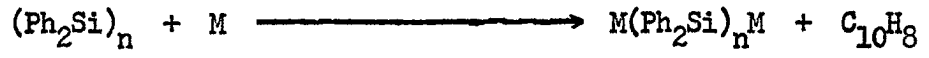
Encouraged by Fearon's success in preparing silylmetallic compound via the reaction of silicon compounds with sodium and lithium naphthalenide, a study was undertaken to determine the general usefulness of such adducts in silicon chemistry. Such an investigation seemed feasible since it is well known (86) that alkali metal-aromatic hydrocarbon adducts may act as reducing agents and since much of silicon chemistry involves reduction with alkali metals.

As a start, the readily reducible phenylated cyclosilanes, octaphenylcyclotetrasilane and decaphenylcyclopentasilane, were treated with lithium and sodium naphthalenide. The reactions were quite facile, resulting in the formation of high yields of the corresponding α,ω-dilithiopolysilanes. Acid hydrolysis or treatment with chlorotrimethylsilane converted these to known compounds. These products were isolated

in 50-65% yields.



Equivalent results were obtained by using catalytic amounts (ca. 7:1 molar ratios) of naphthalene or biphenyl in the presence of excess metal.



Unlike lithium (in THF), sodium metal does not cleave silicon-silicon bonds, thus no previous attempts had been made to prepare the α,ω-disodiopolysilanes. Consequently, the procedure presented here represent the only available routes to these sodium derivatives. On the other hand, the silyllithium compounds have been prepared by lithium cleavage of the corresponding cyclosilanes (4). The methods given here for 1,5-dilithiodecaphenylpentasilane offer no preparative advantages since this compound can be conveniently prepared in 80% yield via lithium cleavage of the cyclosilane (4,84). 1,4-Dilithiooctaphenyltetrasilane, however, was prepared in only 27 to 35% yields (87,88). The method developed in this study then represents an improved procedure for the synthesis of this compound.

The mechanism which best correlates the data obtained, especially the recovery of naphthalene, is one involving the transfer of one or more electrons to silicon followed by rupture of the ring.

$$(Ph_2Si)_4 + C_{10}H_8\cdot\bar{M}^+ \longrightarrow (Ph_2Si)_4\cdot\bar{M}^+ + C_{10}H_8$$

$$\downarrow$$

$$C_{10}H_8 + M(Ph_2Si)_4M \xleftarrow{C_{10}H_8\cdot\bar{M}^+} Ph_2\dot{S}i(Ph_2Si)_2\bar{S}iPh_2M^+$$

Next, we decided to determine if dodecamethylcyclohexasilane (XVIII) would undergo a similar reaction to give a 1,6-dimetallic compound. A 2:1 molar ratio of sodium naphthalenide and this cyclopolysilane gave a high recover of unchanged starting material; however, there was evidence that some cleavage occurred. More success was realized when the lithium-biphenyl system was employed. Under the conditions given in the Experimental part, mixtures of silanyllithium compounds were obtained, and surprisingly, the major products contained more than six silicon atoms. The mixture from one experiment was hydrolyzed to give a large number of silicon hydrides and an insoluble dimethylsilyl polymer. The compounds

$$(Me_2Si)_6 + Li \xrightarrow{C_{12}H_{10}} Li(Me_2Si)_nLi$$

$$Li(Me_2Si)_nLi \xrightarrow{H_3O^+} H(Me_2Si)_nH + \text{Polymer} \quad (n \geq 3)$$

with n = 3-6 were identified by v.p.c.

Further evidence for polymerization and the existence of the silyllithium compounds was obtained from subsequent runs. The mixtures were treated with chlorotrimethylsilane or chloropentamethyldisilane to give permethylated polysilanes.

$$Li(Me_2Si)_nLi \xrightarrow{Me_3SiCl} Me(Me_2Si)_nMe + \text{Polymer} \quad (n \geq 5)$$

The compounds with n = 5-11 were identified by v.p.c. and indirect evidence was obtained (see Experimental) for higher homologs. Small amounts of the compounds with n = 10 and 12 were isolated and identified by melting and mixed melting points.

These results may be explained by a mechanism similar to that given for the phenylated cyclosilanes. The polymerization may be readily explained in terms of radical coupling and/or ring cleavage by silanions or silyl radicals.

$$(Me_2Si)_6 + LiMe_2Si(Me_2Si)_nSiMe_2Li \longrightarrow LiMe_2Si(Me_2Si)_{n+6}SiMe_2Li$$

Since attempts to prepare alkylsilyllithium compounds <u>via</u> lithium cleavage of Si-Si bonds were unsuccessful (discussed in the Historical section), it was desirable to determine if this method involving alkali metal-hydrocarbon adducts would prove to be suitable for the preparation of such compounds. The reaction of sodium naphthalenide with hexakis(trimethylsilyl)disilane appeared to be a good starting point since this polysilane reacts rapidly with lithium. Upon running the experiment, a facile reaction occurred giving as the major product, tris(trimethylsilyl)silylsodium which was converted to tris(trimethylsilyl)silane by acid hydrolysis. The latter was readily identified by v.p.c.

$$(Me_3Si)_6Si_2 + C_{10}H_8{\cdot}Na^+ \longrightarrow (Me_3Si)_3SiNa + (Me_3Si)_4Si$$

$$(Me_3Si)_3SiNa \xrightarrow{H_3O^+} (Me_3Si)_3SiH$$

Small quantities of three other products were detected by v.p.c. One of these was identified as tetrakis(trimethylsilyl)silane.

When an excess of lithium naphthalenide was used instead of the sodium adduct, and the resulting solution was derivatized with chlorotriphenylsilane, the expected tris(trimethylsilyl)(triphenylsilyl)silane was isolated in high yield.

$$(Me_3Si)_6Si_2 + C_{10}H_8{\cdot}Li^+ \longrightarrow (Me_3Si)_3Li$$

$$(Me_3Si)_3SiLi + Ph_3SiCl \longrightarrow (Me_3Si)_3SiSiPh_3 \quad 75\%$$

Having shown that an alkalyted polysilanylmetallic compound can be formed by the reaction given above, the technique was then extended to the preparation of tris(trimethylsilyl)silyllithium and tris(trimethylsilyl)silylsodium from tetrakis(trimethylsilyl)silane. These experiments were carried out with excess metal in the presence of small amounts of naphthalene or biphenyl.

$$(Me_3Si)_4Si + (XS)M \longrightarrow (Me_3Si)_3SiM + \text{By-products}$$

M = Li and Na

These species were characterized by derivatization with a number of reagents as shown in the Experimental section (p. 95 Table 11). Acid hydrolysis and treatment with chlorotrimethylsilane showed that the silylmetallic compounds were present in 80-90% yield. The reasons for the drop in yields when phenyl-substituted chlorosilanes were used as derivatizing agents were not clear. However, this may be associated with the presence of active aromatic compounds which might have reacted with the products.

The effect of hydrocarbons was found not to be completely catalytic as with the phenylated cyclic silicon compounds and a 4:1 molar ratio of polysilane (XI) to hydrocarbon was required to complete the reactions. This may be associated with the fact that the hydrocarbons were converted to trimethylsilyl aromatic compounds which were probably ineffective in causing the desired cleavage. One such compound, 4,4'-bis(trimethylsilyl)-diphenyl was isolated from two of the reactions in which biphenyl was employed.

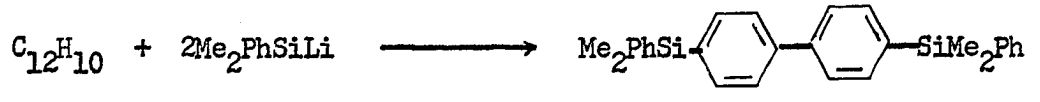
Trimethylsilane and hexamethyldisilane were also determined to be byproducts of the reactions. The former was collected in a cold trap and identified by its infrared spectrum. Hexamethyldisilane was detected by v.p.c.

Biphenyl was preferred over naphthalene, initially because it was easier to follow (by v.p.c.) the disappearance of the starting material and the formation of the silylmetallic compounds. The latter were converted, by acid hydrolysis, to the silicon hydride XVII which had about the same retention time as naphthalene and the dihydronaphthalenes. It was also determined that fewer byproducts were formed when biphenyl was used.

Although tris(trimethylsilyl)silyllithium can be conveniently prepared in high yield (ca. 90%) via the treatment of tetrakis(trimethylsilyl)silane, the method presented here does offer some obvious advantages in terms of the number of steps involved and the quantity of materials required. The only disadvantages are afforded by the presence of relatively small amounts of basic species other than the silylmetallic compounds and the presence of byproducts which would have the expected

effect on the purification of products. The data given in Table 11 show that the effects of these are not so important as to make the preparation of tris(trimethylsilyl)silyllithium by this method impractical. No difficulties were encountered in obtaining pure tris(trimethylsilyl)-silane (XVII) when the silylmetallic compounds were hydrolyzed. For the reasons given above, naphthalene was not used in the preparations of XVII. It is also significant that the yields of XVII (ca. 90%) are equivalent to those obtained when the silyllithium compound (XIX) was prepared by the treatment of tetrakis(trimethylsilyl)silane with methyllithium.

The reaction path(s) involved in these experiments with tetrakis-(trimethylsilyl)silane are not as obvious as that for the phenylated polysilanes. The difficulty is caused by the isolation of 4,4'-bis(trimethylsilyl)diphenyl. This product could have been formed by nucleophilic attack on a trimethylsilyl group or by the addition of a silanion (or radical) to the aromatic nucleus. Fearon[1] showed that this latter type reaction occurs when biphenyl is treated with dimethylphenylsilyllithium.



The required ratio of reactants (4:1), and the formation of triphenylsilane and hexamethyldisilane clearly indicate that the mechanism

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[1] F. W. G. Fearon, Iowa State University of Science and Technology, Ames, Iowa. Information on the reaction of dimethylphenylsilyllithium with biphenyl. Private communication. 1966.

does not involve nucleophilic attack alone as when methyllithium is employed. Thus, the combined data indicate that the reaction proceeds, at least in part, by electron transfer to silicon as shown below. The second step may involve paths (a) and/or (b).

$$(Me_3Si)_4Si + C_{12}H_{10}{}^{\bullet}M^+ \longrightarrow (Me_3Si)_4Si{}^{\bullet}M^+$$

$$(Me_3Si)_4{}^{\bullet}M^+ \xrightarrow{(a)} (Me_3Si)_3S\bar{i}M^+ + Me_3Si\cdot$$

$$(Me_3Si)_4{}^{\bullet}M^+ \xrightarrow{(b)} (Me_3Si)_3Si\cdot + Me_3S\bar{i}M^+$$

$$(Me_3Si)_3Si\cdot \xrightarrow[\text{or Li}]{C_{12}H_{10}{}^{\bullet}M^+} (Me_3Si)_3S\bar{i}M^+$$

Larger quantities of biphenyl were ineffective in causing cleavage of a second trimethylsilyl group to give a dilithium compound.

This method was subsequently extended to the preparation of other silylmetallic compounds as shown below.

$$(Me_3Si)_3SiMe + M \xrightarrow{C_{12}H_{10}} (Me_3Si)_2MeSiM$$

M = Li
M = Na

$$(Me_3Si)_2SiMe_2 + Li \xrightarrow{C_{12}H_{10}} Me_3SiMe_2SiLi$$

35-40%

Bis(trimethylsilyl)silyllithium (XII) and the corresponding sodium compound were derivatized with chlorotriphenylsilane to obtain the known compound, bis(trimethylsilyl)(triphenylsilyl)methylsilane (79).

The reactions involving the preparation of pentamethyldisilanyllithium gave complex mixtures of basic compounds that were derivatized with chlorodimethylphenylsilane and chlorodimethylsilane. The expected

trisilanes were identified by their v.p.c. retention times and by infrared analysis. These were estimated to be present in 35-40% yield.

$$Me_3SiSiMe_2Li \xrightarrow{PhMe_2SiCl} Me_3SiSiMe_2SiMe_2Ph + \text{Others}$$

$$Me_3SiSiMe_2Li \xrightarrow{HMe_2SiCl} Me_3SiSiMe_2SiMe_2H + \text{Others}$$

Evidence was also obtained for the presence of higher polysilanes which may have been formed by the coupling of silyl radicals.

The fact that this silyllithium compound was obtained in low yields tends to indicate that it is highly reactive and relatively unstable. This would be in agreement with earlier reports (see the Historical section) that the stability of methylated silyllithium compounds is a function of branching in the molecule. It is also significant that longer periods of time were required to complete the preparation of the primary silyllithium compound, pentamethyldisilanyllithium.

Under these conditions, sym-tetrakis(trimethylsilyl)dimethyldisilane (XXVIII) gave products resulting from cleavage of the symmetrical and peripheral Si-Si bonds. Acid hydrolysis converted the two silyllithium compound to the known silicon hydrides which were readily identified

$$\underset{\text{XXVIII}}{(Me_3Si)_2MeSiSiMe(SiMe_3)} + Li \xrightarrow{C_{12}H_{10}} \underset{\text{XXII}}{(Me_3Si)_2MeSiLi} + (Me_3Si)_2MeSiSiMe(SiMe)Li$$

by v.p.c.

It is possible that the lithium-biphenyl adduct only caused cleavage of the symmetrical Si-Si bond to give bis(trimethylsilyl)methylsilyllithium (XXII). The second silyllithium compound then could have been formed by attack of XXII on the starting material (XXVIII) and the re-

sulting tris(trimethylsilyl)methylsilane could have been converted to XXII

$$\text{XXII} + \text{XXVIII} \longrightarrow (Me_3Si)_3SiMe + (Me_3Si)_2MeSiSiMe(SiMe_3)Li$$

as discussed earlier. This mechanism is consistent with that given earlier to explain the formation of tetrakis(trimethylsilyl)silane when hexakis(trimethylsilyl)disilane was treated with sodium naphthalenide.

Finally, bis(trimethylsilyl)phenylsilyllithium was prepared by the reaction of tris(trimethylsilyl)phenylsilane with the lithium-biphenyl adduct.

$$(Me_3Si)_3SiPh + Li \longrightarrow (Me_3Si)_2PhSiLi$$

$$(Me_3Si)_2PhSiLi + Ph_3SiCl \longrightarrow (Me_3Si)_2PhSiSiPh_3 \quad (40\%)$$

Treatment with chlorotriphenylsilane gave bis(trimethylsilyl)(triphenylsilyl)phenylsilane. This silyllithium compound was previously prepared by the cleavage of a Si-Ph bond in bis(trimethylsilyl)diphenylsilane as discussed in the Historical section.

V.p.c. evidence indicated that the reaction of tris(trimethylsilyl)-phenylsilane with the lithium-biphenyl adduct also caused cleavage of the Si-Ph bond to give about a 15% yield of tris(trimethylsilyl)silyllithium. Details of this evidence are given in the Experimental section.

Physical and Spectral Properties

A detailed study on the effect of branching on physical and spectral properties of polysilanes was not undertaken; however, it is noteworthy that the available data support previous reports (see Historical section) that branched-chain compounds have higher melting points and are more

volatile than their linear isomers. Table 13 gives data for some branched (B) and linear (L) compounds that illustrate these effects.

Table 13 also gives ultraviolet spectral data that substantiate earlier reports (given in the Historical section) that branched polysilanes absorb at lower wavelenghts than their corresponding linear analogs.

The last four compounds listed in the Table show the effect of substituents such as hydrogen, methyl, chloro- and hydroxyl- on the position of maximum absorption in some branched compounds. It is especially noteworthy that the presence of chloro- and hydroxyl- more than offset the effect of branching and causes the λ_{max} to shift to a value greater than that for the corresponding phenyl compound. This possibly suggests that pπ-dπ bonding with the non-bonding electrons is greater than that involving the π electrons of phenyl.

Previous studies with linear compounds indicated that substituents such as chloro- hydroxyl and H- have little effect on the band position (see the Historical section).

Table 13. Physical and Ultraviolet Spectral Data for Some Linear and Branched Polysilanes

	Compound	M.p. (°C)	λ_{max} (mμ)
B	$(Me_3Si)_2MeSiSiMe(SiMe_3)_2$	147-149 (Sublimes)	None above 210
L	$Me(Me_2Si)_6Me$	liquid (36)	260 (41)

Table 13. (cOntinued)

	Compound	M.p. (°C)	λ_{max} (mμ)
B	$(Me_3Si)_2PhSiSiPh(SiMe_3)_2$	374-378 (Sublimes)	235 (sh)
L	$Ph(Me_2Si)_6Ph$	86-87 (89)	265 (45)
B	$(Me_3Si)_3SiSi(SiMe_3)_3$	ca. 374-379dec. (Sublimes)	None above 210
L	$Me(Me_2Si)_8Me$	61 (36)	272 (41)
B	$(Me_3Si)_3SiPh$	———	241 (19)
B	$(Me_3Si)_3SiH$	———	None above 210 (18)
B	$(Me_3Si)_3SiMe$	———	209(sh) (18)
B	$(Me_3Si)_3SiCl$	———	250
B	$(Me_3Si)_3SiOH$	———	250

Suggestions for Further Research

In the interest of extending investigations in the field of branched-chain silicon chemistry, the one-step synthetic procedure should be extended to the preparation of other tri- and tetrasilyl-substituted silanes. This would be particularily desirable since a number of monochloroalkylsilanes are available for use in addition to chlorodimethylsilane and chlorotrimethylsilane. Trichlorosilanes other than methyl- and phenyltrichlorosilane should also be employed.

The lithium-THF system should also be investigated for general use in the coupling of alkylhalosilanes since this method would have several obvious advantages over the use of sodium and sodium-potassium alloy.

Preliminary studies indicated that compounds of the type: $H(Me_2Si)_n Cl$, may be prepared in high yield by the reaction of α,ω-dihydropolysilanes with carbon tetrachloride. This method should be investigated as an alternate route to these compounds. The procedure would involve chloronation of dodecamethylcyclohexasilane to give a mixture of α,ω-dichloropolysilanes. Without separation, these should be reduced to the corresponding silicon hydrides which are purified more conveniently. The desired α-chloro-ω-hydropolysilane could then be prepared by treating the appropiate compound with carbon tetrachloride.

The present method involves hydrochlorination of dodecamethylcyclohexasilane under pressure, yielding a complex mixture of twelve compounds (90). In addition to avoiding a tedious separation, no special equipment would be required for the proposed method and larger quantities of a given product would be obtained.

Now that polysilanes containing dimethylsilyl (HMe_2Si) groups may be readily prepared by a one-step procedure, the reaction of these with carbon tetrachloride should be investigated for the introduction of one or more chlorine atoms.

Since the silicon-silicon bonds of tetrakis(trimethylsilyl)silane are cleaved relatively slowly by halogenating reagents, the chlorination of this polysilane under free radical conditions should be investigated as a means of forming compounds containing chloromethyl ($ClCH_2$-) groups. Kumada's method for the preparation of chloromethylpentamethyldisilane

from hexamethyldisilane (91) may prove to be satisfactory.

Some polychlorosilanes, $R_{4-n}SiCl_n$, should be treated with less than n equivalents of tris(trimethylsilyl)silyllithium at ca. -70°. To facilitate the purification of products, it may be advisable to convert the resulting chlorosilanes to the hydrides by treatment with lithium aluminum hydride. These reactions should afford some interesting highly-branched compounds containing functional groups.

Comparative studies should be undertaken to determine if there are any advantages in using the available silylsodium compounds instead of their lithium analogs. Also, the method of synthesis described here should be extended to the preparation of some compounds containing other alkali metals. Although the preparation of these for general use may be impractical, these may be used for theoretical studies such as the determination of the relative ionic character of the Si-M bonds.

The reaction of dodecamethylcyclohexasilane with lithium and biphenyl, followed by acid hydrolysis, should be run on a larger scale and an attempt should be made to isolate some of the undescribed compounds $H(Me_2Si)_nH$, where $n > 6$.

A study should be undertaken to determine if alkali metal- aromatic adducts may be used for reductive coupling of chlorosilanes.

SUMMARY

A review of the chemistry of branched-chain polysilanes and the reactions of anion radicals with organosilicon compounds was presented.

Octamethyltrisilane and 2-ethylheptamethyltrisilane were prepared in high yield by a one-step procedure involving the reaction of dichlorodimethylsilane and methylethyldichlorosilane with lithium and chlorotrimethylsilane in THF. sym-Tetrakis(trimethylsilyl)dimethyldisilane a highly branched polysilane was isolated incidental to the preparation of tris(trimethylsilyl)methylsilane from methyltrichlorosilane, lithium and chlorotrimethylsilane.

When attempts were made to use this method for the preparation of trimethylsilyl-substituted phenylsilanes, compounds resulting from reduction of the phenyl groups were obtained as major products. These were determined to be 3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-ylsilanes. A number of compounds of this type were prepared to show that the reaction is general for phenyl-substituted monosilanes and phenyl-substituted polysilanes in which the Si-Si bonds are not readily cleaved by lithium. Optimum conditions were determined for the preparation of tris(trimethylsilyl)(3,4,5,6-tetrakis(trimethylsilyl)cyclohexen-1-yl)-silane from phenyltrichlorosilane.

A satisfactory procedure, involving the use of a mixture of ether and THF as solvent, was developed for a one-step preparation of some trimethylsilyl-substituted linear and branched phenylsilanes.

Hexakis(trimethylsilyl)disilane (XXXIII) a novel, highly branched and symmetrical organopolysilanes was prepared by a number of methods.

The reaction of tris(trimethylsilyl)silyllithium with 1,2-dibromoethane at ca. -70° afforded 40-50% yields of this compound and proved to be the best method of preparation.

Cleavage of the symmetrical Si-Si bond occurred when hexakis(trimethylsilyl)disilane (XXXIII) was treated with lithium, methyllithium and sodium naphthalenide. Treatment of XXXIII with tris(trimethylsilyl)-silyllithium, triphenylsilyllithium, chlorine and bromine caused cleavage of peripheral Si-Si bonds.

Tris(trimethylsilyl)silane (XVII) was found to react spontaneously and rapidly with carbon tetrachloride affording very high yields (87-92%) of tris(trimethylsilyl)chlorosilane. The latter was also prepared by the reaction of tris(trimethylsilyl)silane (XVII) with phosphorus pentachloride.

Tris(trimethylsilyl)bromosilane was prepared by the reaction of XVII with 1-bromobutane. Attempts to prepare this bromosilane and the corresponding chlorosilane by halogenation of tetrakis(trimethylsilyl)-silane gave compounds resulting from cleavage of two and three trimethylsilyl groups as major products.

Preparation of a number of other branched and linear chlorosilanes are described. Also, it was determined that a number of available silicon hydrides react with carbon tetrachloride to give chlorosilanes.

Attempts to prepare some highly branched compounds by the reaction of tris(trimethylsilyl)silyllithium with hexachlorodisilane, methyltrichlorosilane and dimethyldichlorosilane at room temperature or 0° gave tetrakis(trimethylsilyl)silane as the only isolable product. More success was obtained when this silyllithium compound was reacted with 1,2-dichloro-

tetramethyldisilane.

The reactions of bis(trimethylsilyl)methylsilyllithium with some dichlorosilanes are described.

Procedures are described for the preparation of some silyllithium and silylsodium compounds in the presence of alkali metal-aromatic hydrocarbon adducts. Many of the silyllithium compounds had been prepared by different procedures; however, the methods given here represent the only means of preparing the sodium compounds. Mechanisms for the formation of the silylmetallic compounds are discussed in terms of electron transfer from the hydrocarbon adduct to silicon.

The lithium-biphenyl adduct reacted with dodecamethylcyclohexasilane to give compounds containing more than six linear silicon atoms. This afforded strong evidence for the existence of intermediate silyl radicals.

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